Puddling: a metallurgical perspective

Merton C Flemings and David V Ragone

ABSTRACT: Puddling was the process of choice for producing wrought iron and steel for most of the 19th century. The original dry puddling process was replaced beginning in 1830 by wet puddling, which was radically different in terms of the key chemical reactions involved, the thermal behaviour of the melt, the speed of the process and the quality and consistency of the resulting product. In this paper we examine wet puddling from a metallurgical perspective and express our respect for those master puddlers who could control such a complex process with little other than their senses to guide them. Concluding remarks relate to the final years of wrought iron production in Great Britain and the United States.

Dry Puddling

The most important development in the technology of producing wrought iron and steel following the invention of coke smelting was puddling. The key initial invention is generally acknowledged to be that of Henry Cort, described in his patents taken out in 1783 and 1784. His process, originally termed puddling, is now generally known as dry puddling to distinguish it from the later development, wet puddling. In dry puddling, wrought iron is produced from cast iron by decarburization in a reverberatory furnace fired with coke. The process involves constant stirring to achieve the decarburization by oxidation from the air. At the end of the decarburization, the iron is in a semi-solid pasty form; the mass is then formed into a ball for subsequent working (Gale 1963, 1–11; Hyde 1994, 254–270; Mott 1983, 37–39; Turner 1895, 347–356. For illustrations of puddling furnaces see Percy 1864, 640–651).

One limitation of dry puddling was that it required the cast–iron charge to be low in silicon. It was slow and wasteful of iron. The sand furnace bottom employed in the operation reacted with iron oxide formed during the melting operation to form an iron-containing slag, so that as much as half the iron charged could be lost in this slag (Gale 1963, 1–11). Nonetheless, the process was a great advance over what had gone before, and after incremental improvements in the process made in the years immediately following its development, widespread adoption began in the mid-1790s, and by 1815 British annual wrought iron output had risen to 150,000 tons, almost a five-fold increase from the production in 1788 of 32,000 tons (Hyde 1994, 254–270).

Wet Puddling

In 1811, Joseph Hall, building on a suggestion of S B Rogers, began experimenting with an iron-oxide furnace bottom, replacing the sand bottom of dry puddling. By 1830 he was able to apply his process commercially. It was spectacularly successful and was to become the predominant means of production in Great Britain for all the years that wrought iron remained a significant engineering material. Only in 1885 did steel output exceed that of wrought iron in Great Britain, and wrought iron continued to be produced commercially until well into the 20th century.

Hall's process represented not only an incremental improvement over the original puddling process, but a major departure in terms of the key chemical reactions involved, the thermal behaviour of the melt, the speed of the process and the quality and consistency of the resulting product. The innovation ranks on a par, surely, with that of Cort's process in terms of its originality and industrial importance. It is referred to today as wet puddling, since it involved much more slag than the earlier process. It has been described in a number of recent and contemporaneous publications, as summarized by Gale (1963, 1–11), Turner (1895, 347–356), Barraclough (1971, 785–789), Morton and Birt (1974, 96–102), and Gordon (1996, 133–135).

Our attention was first drawn to this process on realizing its apparently unique nature: that the driving force for the chemical refining is directly impacted by crystallization of the iron. Thus, one purpose of the study was to satisfy our own curiosity. Beyond that, we hope that the resulting paper will demonstrate how remarkable the puddling development of 1830 was, building as it did on the work of others over the previous century, combining a number of non-obvious essential elements, and permitting large-scale manufacture of high quality iron by artisans without recourse to modern means of sensing and control.

Melting and rabbling

As is to be expected, details of wet-puddling practice changed somewhat over time and differed from location to location. Differences, for example, were in furnace size, components of the furnace lining (the 'fettling'), and when and if additions were made during the process. Comparison of descriptions of puddling dating to the 1870s with those of the early years of the 20th century, indicates a significant increase in heat size, and decrease in cycle time. Nonetheless, the furnace design and puddling process were essentially unchanged, including a furnace lining containing a high percentage of iron oxide, a cooled metal base plate on which the furnace lining rested, and a vigorous boil during the carbon reduction stage.

Several eyewitness accounts of puddling in the early to middle years of the 20th century provide an excellent overview of the process. Gale (1963, 1–11) and Morton and Birt (1974), have given first-hand detailed accounts of puddling in Great Britain, and Davis (1922, 38–47) has done the same for puddling in the United States. In addition, Gordon (1996, 133–135), a steel reference book (United States Steel Company 1985) and Bray (1942, 200–213) have summarized accounts of others. There now follows a summary of the operation which would have been seen in an iron works during these later years of puddling, based on the accounts of Gordon, Bray and Davis.

The puddler first fires his reverberatory furnace, capable of handling a 600lb (*c* 270kg) charge of cast iron. A furnace lining comprising largely Fe_3O_4 forms the melting basin. It is sintered to form a monolithic structure, with the aid of added iron or slag. The lining rests on an air-cooled iron base.

To start a heat, the puddler shovels 500–600lb (*c* 230-270kg) of pig iron into the furnace, and also adds some mill scale (iron oxide). He and his helper then do their best to seal all openings, to minimize entrance of oxygen to the furnace interior, and open the damper to get maximum heating and minimum oxidation of the melting iron. Charging the furnace takes about two minutes, the heating and melting another 30 minutes. The puddler then lowers the damper to keep heat input low and make the atmosphere less oxidizing, while his helper begins to stir the metal, the better to expose it to the oxide-rich slag which has formed. This step of the process, called 'learing', takes eight or ten minutes and removes much of the silicon and phosphorus. When the puddler sees a subtle change in colour of the metal from a reddish to a bluish hue, he knows that as much of the phosphorus as possible has been removed. This step has taken about ten minutes.

The boil

As soon as the metal has 'cleared,' the puddler brings on the boil by adding some mill scale. To keep the phosphorus from reverting to the metal, he initially maintains a smoky, reducing atmosphere by keeping the damper low. The bath is hard to stir, but after about 10 minutes of strenuous stirring, the bath becomes more fluid. Carbon in the pig iron begins to oxidize. The slag is somewhat viscous; it begins to foam and rise in the furnace and is permitted to flow freely out of the furnace. The low boil has begun.

After sufficient depletion of the carbon content, iron begins to solidify, carbon elimination becomes more rapid, the temperature rises and the gas escapes in larger bubbles and burns in small flames called 'puddler's candles'. This is the high boil. In the words of Davis:

> 'This formation of gas in the molten puddle causes the whole charge to boil up like an ice cream soda. The slag overflows. Redder than strawberry syrup and as hot as the fiery lake in Hades it flows to the rim of the hearth and out through the slag hole. My helper has pushed up a buggy there to receive it. More than an eighth and sometimes a quarter of the pig iron flows off in the slag and is carted away. Meanwhile I have

> got the job of my life on my hands. I must stir the boiling mess with all the strength of my body'.

The puddler increases the stirring of the bath while decreasing the heat until the metal 'comes to nature.' Again, in Davis' words,

> 'Little spikes of pure iron like frost spars glow white-hot and stick out of the churning slag. These must be stirred under at once; the long stream of the flame from the grate plays over the puddle, and the pure iron if lapped by these gases would be burned up. Pasty masses of iron form at the bottom of the puddle. These would stick and become chilled if they were not constantly stirred. The whole charge must be mixed and mixed as it steadily thickens so that it will be uniform throughout'.

As the reaction nears completion it becomes pasty and hard to work. The change occurs rapidly, over a period of six to eight minutes. With the elimination of the carbon nearly complete, the boiling subsides and the apparent volume of the slag decreases, called 'the drop' by puddlers. Grains of iron, each enveloped in slag, appear as clusters as the slag drains away from the surface. The metal has 'come to nature', and is ready for balling.

Final steps

With the temperature below the melting point of iron, the puddler next separates the pasty mass of metal and slag into three balls, transports them with the aid of his helper to a 'squeezer', where much of the slag is removed. Then, after shaping and passing the metal through a series of roughing- and finishing-rolls, the resulting product is 'muck bars,' iron bars ¾ inches thick, by two and a half to eight inches wide, by 15–30 feet long. Typically, these muck bars were cut into lengths two to four feet long for subsequent processing.

A puddling model

The clearing and boiling stages of the wet puddling process take place sufficiently rapidly that a useful way to think about them is to assume reactions take place adiabatically. For illustrative purposes, and for comparison with actual practice, consider a cast-iron charge of initial composition 3.0wt% carbon and 1.4wt% silicon at meltdown. The small amounts of other impurities present (Mn, S, P) do not in practice affect the heat balance significantly in the refining. A slag comprising 20% of the weight of the metal charge is assumed.

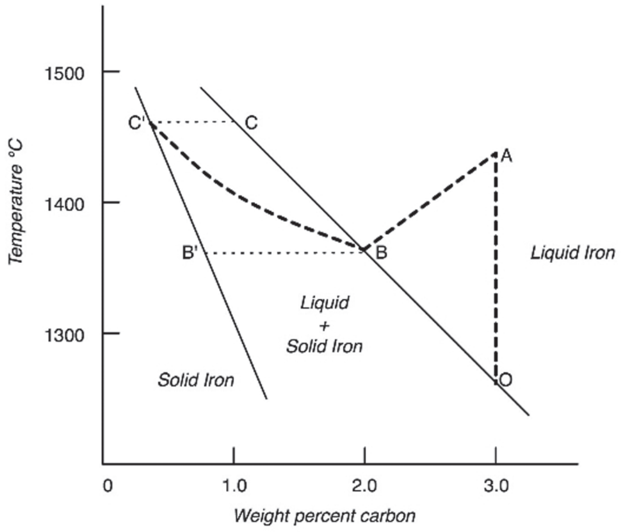

Figure 1: Temperature of the melt during wet puddling, superimposed on a portion of the iron-carbon phase diagram.

After melting, the melt is taken to above its liquidus temperature (Point O, Fig 1) and gentle stirring is begun to initiate 'clearing'. Silicon removal commences, primarily by the reaction:

$$\underline{Si} + 2FeO = SiO_2(liq) + 2Fe(liq) \tag{1}$$

where $\underline{Si}$ represents silicon in an iron solution and $SiO_2(liq)$ represents silica dissolved in the slag. This reaction is exothermic, taking place over approximately 10 minutes, and the temperature rises to point 'A' on the iron-carbon phase diagram of Figure 1.

A small amount of roll scale is next added to help initiate the carbon boil. Carbon removal begins by the endothermic reaction:

$$FeO(liq) + \underline{C} = CO + Fe(liq) \tag{2}$$

where $\underline{C}$ represents carbon in an iron solution. Thus, temperature declines while carbon is being removed. This is shown by the line AB in Figure 1. We conclude that this portion of the boiling corresponds with the low boil referred to in the early puddling literature.

Once the reaction path intersects the liquidus, further carbon removal requires solidification of iron, since at any given temperature, the liquid composition would otherwise move leftward on the phase diagram of Figure 1 into the two-phase region and be 'undercooled'. The overall heat balance is now exothermic due to the heat of solidification; hence, the temperature rises while solidification of iron, and carbon removal, take place simultaneously. The composition of the liquid moves along the liquidus line, following the line BC, and the solid follows along the solidus, B'C'. The average composition of the liquid and solid moves along the line BC$'$.

This period of simultaneous iron solidification, carbon removal and temperature rise, we conclude, corresponds with the period of the high boil referred to in the early literature. The sudden change from the slow gas evolution and temperature decrease during the low boil results from the many gas nucleation sites provided by the solidifying iron, and by the exothermic nature of the overall reaction when iron solidification take place.

The high boil ceases when the iron is fully solidified; this occurs when the reaction path has reached the solidus, (point C$'$, Fig1). At this point, the solid still contains some dissolved carbon. If, however, the master puddler has done his job properly, the carbon level is not much above that aimed for in the wrought iron. Carbon removal from the iron then continues, at a much slower rate, during the balling and initial shaping stages since the iron particles, which are anticipated to be quite small, are embedded in an oxidizing slag, and the carbon in iron diffuses rapidly at these high temperatures.

In a separate paper (Flemings and Ragone forthcoming) we apply modern thermodynamic and solidification theory to the qualitative model described above. To give the reader a sense of the magnitude of these temperature changes, the calculations yield the following: taking Point O as 1260^{0}C (just above the liquidus of the 3.0wt% C and 1.4wt.% Si alloy), the temperature rises to 1392^{0}C at Point A, drops to 1338^{0}C and 2.06wt% C at the intersection with the solidus and then rises during the high boil to 1475^{0}C, with carbon reduced to 0.29%.

We have found no experimental temperature measurements of the metal-bath temperature during the puddling process. Although crude optical pyrometers were in use early in the 20th century, we have as yet found no evidence of their application to puddling. Their use would in any case have been limited, due to the smoky environment of the furnace during operation. One thing which seems clear, however, is that when old puddling records speak of ‘cooling the metal’, or ‘increasing the temperature’ of the metal, these phrases are better read as ‘decreasing heat input to the metal’, or ‘increasing heat input to the metal’, since no temperature measurements were made, and the reactions themselves were producing internal heating or cooling.

Flow of heat into or out of the metal charge would, of course, either accentuate or ameliorate the temperature changes described above. However, we calculate that these heat flows are small (Flemings 1991, 957–981). Rate of heat extraction is limited by the need to maintain a protective atmosphere in the furnace. Rate of heat input is limited by the fact that maximum furnace temperature attained, even in these later days of puddling, was 1430–1450^{0}C (Morton and Birt 1974, 96–102).

Rheology during the high boil

The bath during the high boil comprises four phases: liquid metal, liquid slag, solid metal and gas. Flow is vigorous due to the boiling and to the manual stirring. We know little about the details of such a complex flow, but can build a qualitative picture. We assume that the two liquids, metal and slag, are intermixed on as fine a scale as the boiling and the manual stirring can achieve. Gas evolution is occurring at the metal-slag interface, and solidification is occurring within the metal phase.

Little information exists about the detailed structure of this four-phase fluid, but Turner (1895, 347–356) writes that slags resulting from overflow during the high boil

> ‘… always contain some shots or granules of metal, which are carried over by the turbulence of the boil, and in some cases examined by the author as much as 16 per cent of metal was found in the form of small globules…’.

Of course, in the lower part of the bath, which does not overflow, the iron content would be much higher.

In the case of semi-solid liquid metals (with no gas or slag present), we do know a good deal about morphology of the metal phase and of the flow characteristics of the resulting ‘slurry,’ as a result of decades of study of ‘semi-solid metal processing’. From this work it is known that vigorous stirring in the initial stages of solidification causes dendrites to break up into fine grains which then grow more-or-less spherically, their size depending only on ripening kinetics and hence on time in the liquid-solid zone (Martinez and Flemings 2005, 36A: 2205; Flemings 1991, 957–981). Hence in a 30-minute boiling time with, say, 20 minutes of that during the solidification stage, the average size of these spheroids would be about 60μm. The flow behaviour of these fine-grained semi-solid alloys is thixotropic; their viscosity depends on shear rate, decreasing with increasing shear rate, and increasing with increasing fraction solid. Figure 2 is an example of viscosity of semi-solid steel alloys at several shear rates, versus fraction solid.

We expect the flow behaviour of the slurry in wet puddling to be similar to the foregoing. The turbulence of the gas

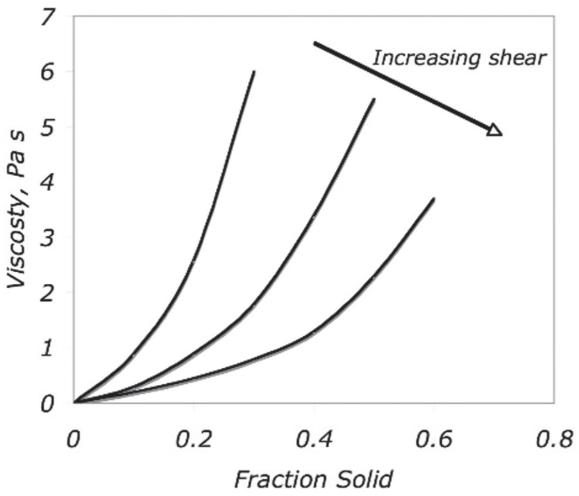

Figure 2: Viscosity versus fraction solid for different shear rates in steel (Flemings 1991).

evolution and the stirring of the puddler not only achieve homogeneity of the bath, but also keep the viscosity of the thixotropic slurry low. Then, as the fraction solid in the slurry increases through solidification of the iron, viscosity gradually increases. At the end of the high boil, gas evolution ceases and the slag level drops, increasing still more the fraction of solid present and hence the viscosity of the slurry. The metal has 'come to nature', the viscosity rises to a high level as the stirring slows, and the puddler 'balls' his agglomerating iron.

The model and the historical record

The model described above agrees in general with the historical record and serves to strengthen our respect for those master puddlers who could control such a complex process with little other than their senses to guide them. The process involves a complex interplay of heat flow, fluid flow, chemical reaction and solidification. Temperature, furnace atmosphere, slag chemistry and amount, stirring and its timing, all needed to be controlled independently with none of the measuring and control tools we have today.

We conclude that the low boil comprises that period of carbon removal before solidification of iron begins; *ie* before the reaction path intersects the liquidus. Then the temperature begins to rise because thermal energy is released during solidification. Also, the solid iron grains provide nuclei for rapid evolution of carbon monoxide. Both factors lead to the high boil. These critical roles of the solidification changing an endothermic process to an exothermic one, and providing heterogeneous nucleation sites, do not appear to be recognized in the literature.

The vigorous action of both puddling and gas evolution results in a degree of homogeneity of the iron not attainable in earlier processes for producing wrought from cast iron. Of equal importance, the fine structure produced permits the process to proceed with great rapidity, both due to the high liquid-solid surface area, and to the very small distances over which carbon needs to diffuse out of the liquid and solid iron phases. Details of the flow behaviour of the four-phase mixture existing during the solidification stage are certainly complex. Nonetheless, results of research on semi-solid forming provide an excellent qualitative understanding of that behaviour as it is reported in the historical literature.

The model and its general agreement with the historic record serve to strengthen the view of the puddling process as a remarkable technological development, employing materials, furnaces and techniques at the then state of the art, and of their practitioners as remarkable in their strength, fortitude and skill. The technological elegance of the wet puddling process leads one to wonder if there may not yet be some practical application of the principles of its operation.

Afterword

Wrought-iron production in both Great Britain and the US peaked somewhere around 1890. Decline thereafter was rapid. By the turn of the century it amounted to only about 15% of the total of wrought iron and steel production in both countries. Wrought iron did not quickly disappear, however. In spite of the lower cost of steel, a market remained for decades because of real or perceived advantages of the wrought product. Some of these were resistance to corrosion, damping capacity, weldability and machinability (Bray 1942, 200–213).

To better compete with steel, a number of furnace and mechanical innovations were introduced to the hand-puddling process in the years up to about 1925. These included double furnaces with enlarged hearths, regenerative and recuperative furnaces, and mechanical devices to reduce labour input. Still, by the mid-1920s wrought-iron bars and shapes were selling in the United States for about 5 cents a pound whereas the price for steel in similar shapes was about 2 cents a pound (Bray 1942, 200–213).

Then in 1920, Dr James Aston at the A M Byers Company in the United States succeeded in bringing about the last great innovation in wrought iron manufacture. In his process, upwards of 2500 pounds (*c* 1140kg) of low-carbon steel, produced in a Bessemer converter, were ladle desulphurised, and then poured into a 'thimble' of molten slag held at a temperature several hundred degrees below the melting point of steel. Vigorous agitation resulted from gas evolution while rapid solidification occurred. The result was a fine mixture of slag and metal, essentially identical to that obtained at the balling stage of puddling. After slag removal, the now-coagulated ball of iron was turned out of the thimble, transported to a squeezer to remove excess slag, and the resulting bloom then rolled in conventional manner. A plant, constructed in 1930, had a daily capacity in excess of 1000 tons of wrought iron produced by this Aston Process (United States Steel 1985, 12–19; Bray 1942, 200–213; Byers 1942, 4–6).

From a metallurgist's point of view, the Aston Process was a quite remarkable development. It was the first (and only) major innovation in wrought iron that resulted from a focused research and development programme employing the best metallurgical understanding of the day. In spite of the fact the process seems to be the result of research working in reverse: starting with steel to produce wrought iron to better compete with steel; it was an economical, high-production process meeting a market need. Finally, even though the puddling and Aston processes are superficially so different, from a thermodynamic and solidification point of view they are remarkably similar and would be described by closely similar mathematical models.

References

A M Byers Company 1942, *General Catalog* (Pittsburgh).

Barraclough K 1971, 'Puddled Steel: a forgotten chapter in the history of steelmaking', *J Iron and Steel Institute* 209, 785–789.

Bray J L 1942, *Ferrous production metallurgy* (New York).

Davis J J 1922, *The iron puddler: my life in the rolling mills and what came of it* (Kessinger Publishing Reprint 2004, Kila, Montana).

Flemings, M C 1991, 'Behavior of metals in the semi-solid state', *Materials and Metals Transactions* 22A, 957–981.

Flemings M C and Ragone D V 2009, 'Puddling: A New Look at an Old Process, to be published in *International Journal of the Iron and Steel Institute, Japan*.

Gale W K V 1963, 'Wrought Iron - A Valediction', *Trans Newcomen Society* XXXVI, 1–11.

Gordon R B 1996, *American iron, 1607–1900* (Baltimore).

Howe H M 1903, *Iron, steel, and other alloys* (Boston).

Hyde C K 1994, 'Technological change in the British wrought iron industry, 1750–1815: A reinterpretation', in Church R A and Wrigley E A (eds) *The Coal and Iron Industries* (Oxford), 254–270.

Martinez R A and Flemings M C 2005, 'Evolution of particle morphology in semi-solid processing', *Materials and Metallurgical Transactions* 36A 2205.

Morton G R and Birt R G 1974, 'The present-day production of wrought iron', *Historical Metallurgy* 8, 96–102.

Mott R A 1983, *Henry Cort: The Great Finer* (ed) Singer P (London).

Percy J 1864, *Metallurgy: vol 2: iron and steel* (London).

Turner T 1895, *The metallurgy of iron. 6th edition* (London).

United States Steel Company 1985, *The making, shaping and treating of steel, 10th Edition* (Pittsburgh).

The authors

Merton C Flemings is Professor of Materials Science and Engineering and Toyota Professor emeritus, Massachusetts of Technology. He has been a member of the faculty of MIT since 1956. His research specialization is metal processing.
Address: Room 4-415, Massachusetts Institute of Technology.Cambridge, MA 02139, USA
e-mail: flemings@mit.edu

David V Ragone is Senior Lecturer (retired) in the Department of Materials Science and Engineering at the Massachusetts Institute of Technology, and President Emeritus of Case Western University. His area of specialization is thermodynamics of materials.
Address: 8 Hillside Road, Wellesley, MA 02481, USA
e-mail: ragone@mit.edu