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An Analysis of the Processes for Smelting Tin

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Abstract

The process for smelting tin, unlike most other commodity metals, has undergone few significant conceptual changes between prehistory and the start of the first World War. The rationale of blast furnace dimensions is presented in the context of early Cornish and more recent practice, together with the metallurgical implications of smelting dirty ores with cast iron as practised in Cornwall with early reverberatory furnaces. Conditions for the operation of arsenic roasters and an overview of impurity removal and slag cleaning techniques are given. Finally, the development of tin smelting flowsheets is traced using examples taken from 16th to 20th *century practice.*

OVERVIEW OF THE EXTRACTION OF TIN FROM CONCENTRATES

'Anyone can smelt tin!' - Brian Earl (Earl 1985) in the first of his comprehensive papers on Cornish tin smelting, states what might appear to be the obvious and then demonstrates (Earl 1986) that it is not as easy as might be expected. It is easy to produce tin from even mediocre concentrates - the only difficulty is to do so economically without throwing most of it away either as slags, scoria, fume or unaccountable losses.

The balance between losses in ore dressing and smelting is one of the eternal problems in tin metallurgy. Fig. 1 shows the amount of waste slag made from 100 tonnes of total furnace charge (which includes recycled materials but not fuel). If low grade concentrates are sent to the smelter:

1. The furnace and staff are being used to produce slag rather than tin.
2. Impurities are present in the gangue rather than the cassiterite - so more impurity is going into less and less metal.
3. Because there is more slag and less metal - smelting losses become greater.

Fig. 2 shows the losses at 15%Sn in slag for a traditional blowing furnace and a mid-C20th two stage smelter with a 2% Sn slag. The model assumes a loss of 10% of all tin as fume and fugitive losses but this is recovered in the modern case. Nevertheless, a loss of 2.5% is fairly average in a well-run smelter today.

The second problem arises from the similarity in reducibility of tin and iron oxides. Here the smelter is faced with the classic Catch 22 situation: If he works his furnace under very reducing conditions to produce a slag with a low tin content, he also produces quantities of iron, which take with them something like nine times their own weight of tin as refining drosses. If he reduces gently then he produces a slag which may have 15-30 % Sn in it even when metallic prills have been taken out. The limit is determined by the amount of iron dross recycle which can be handled. Several smelting works in the 20th century have bought a little too many medium grade concentrates and found that they have large quantities of dross which either recycles unproductively or must be stockpiled waiting for a better day. The answer of course is to produce the highest grade of concentrate possible but this is done at the expense of disproportionately high ore dressing losses. The poor miner, therefore, has to judge whether he will throw much of his hard won tin away as dressing losses or pay a smelter an exorbitant charge to do that for him.

The processes which are important for tin are: smelting, refining and slag cleaning. These are summarised in Fig. 3 and it will be seen that with the exception of the introduction of the reverberatory furnace and the refining kettle or pot, there has been very little change between prehistory and the 20th century.

PROCESSES FOR SMELTING

Blast Furnaces

The European furnaces, described by Agricola (Agricola 1556), were almost identical with those used in Saxony during the late 19th century (Louis 1911). Both had two tuyeres with similar dimensions (8 to 9 feet high, 2 feet long and one foot wide for the upper part and less near the tuyeres). The method of construction with a massive sandstone hearth and walls of sandstone or granite, lined with clay lute are also similar. The external forehearth has changed in detail over three centuries. The bellows were powered by a waterwheel, although Agricola also describes smaller furnaces used in Lusitania, blown by hand-bellows.

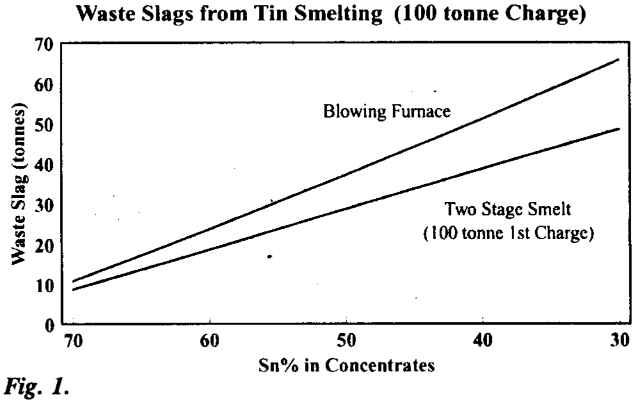

Fig. 1.

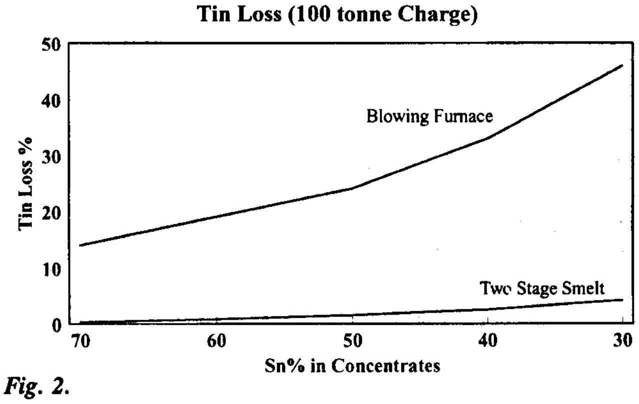

Fig. 2.

Barba writing in 1637, duplicates Agricola in several respects, suggesting either a common source of literature or of smelting practice. For example, both refer to tin blast furnaces as being smaller than those for smelting other ores, the need to blow gently, the use of sandstone for the hearth, the need to remove stones from both concentrates and charcoal and the use of charcoal to cover the surface of molten tin to prevent oxidation.

Biringuccio (1540) and Ercker (1574) appear to have had little experience with tin concentrate smelting although Ercker refers to the recovery of old tin slags.

Louis (1911) describes all the types of tin blast furnace throughout the world at the end of the 19th century. His book, based on an earlier monograph, is a compilation of personal observations, papers and in some cases government sponsored smelting trials in south east Asia and has been repeated verbatim by Thibault (1908). He later gives quantitative information on the continuous operation of primitive single tuyere furnaces, many of which, were blown with hand blowers made from hollow logs. There is a wealth of experimental detail in Louis' account which is directly relevant to any simple shaft furnace working on tin concentrates with charcoal as fuel.

Dimensionally, the furnaces described by Louis are similar to those of Agricola and Pryce (1778). They range from just under 1 m in height to nearly 3m. Those with square shafts have a limiting dimension of about 0.7 m which is also the limiting dimension of the slag hearths used for lead in the North of England. The limiting dimension of about 0.7m is interesting in that it is also the maximum diameter of the cylindrical shaft furnaces used in south east Asia, also described by Louis; furthermore it is a significant empirical dimension in many modern non-ferrous blast furnaces.

At Capper Pass, North Ferriby in Humberside (the UK's last tin smelter) the blast furnaces were rectangular with several tuyeres (six, ten and fourteen for the three furnaces last in use); the separation between opposite tuyeres was 1.8m and adjacent tuyeres were spaced at 0.7m centres. Elkington's secondary copper blast furnace had a width of 1.3m between opposing tuyeres and a spacing of 0.9m between adjacent tuyeres.

The lead blast furnace at Herculaneum had a width of 1.7m but the tuyeres were very close together (0.4m) as is usual with large lead furnaces. It was generally held that these dimensions were determined by the limit of penetration of an air stream into a hot coke bed and were composed of elements equivalent to several single tuyere furnaces. This means that the Capper Pass furnaces were in fact an assemblage of single tuyere equivalents of 0.9m by 0.7m; and are shown in Fig.4 Elkington's secondary copper furnace was made up of units 0.65m by 0.9m and the Herculaneum lead furnace 0.85m by 0.4m. (Ironmaking blast furnaces are circular in section and have much wider dimensions than these. However, they work in a different way with a so-called 'dead man' of quiescent coke in the centre which acts as a holding medium for metal and slag). Clearly it is possible to have smaller dimensions, for example the Spanish and Mexican furnaces described by Louis with shaft diameters of 0.2m. If these dimensions of 0.7m are substantially exceeded then the resulting furnace can be expected to show dead spots, first at the corners and then at the walls in extreme cases. These dimensions seem to have been arrived at through years of unrecorded experience and it may be that they have been critically derived to give maximum smelting area at the same time as affording a degree of protection to the walls of brick or refractory furnaces. This could have been done by inspection in an early single tuyere furnace but would have been impossible in a modern water-jacketed unit with a height of 5-8m.

Another feature of non-ferrous blast furnaces is that the hearth can become accreted and prevent metal and slag escaping through the taphole. This is particularly noticeable with tin or tin alloy furnaces (where iron is also reduced) or if zinc sulphide is present. If the charge produces a very high metal fall and only little slag, the problem can be acute. It is easily overcome by re-running good slags and although this is an apparently unprofitable burden, the practice can actually increase throughput rates. This was normal, with large furnaces in the 20th century, as at the Capper Pass smelter, where slag was added to lead- and copper-alloy charges which had a shortage of gangue. It would be very beneficial in a short blast furnace where there is little residence time and where it would help with slag formation, particularly if additives such as chalk or lime were used. None of the early Cornish writers (ie Beare 1586; Carew 1602; Cotton 1664; Anon 1671) refer to the incorporation of slag in the charge, although this would be less important for early Cornish furnaces working for a 'tide' of twelve hours. It was normal practice with several of the simple furnaces described by Louis (1911) and is referred to by Agricola, both of whom describe smelting campaign lasting several days.

Perhaps ironically, the blast furnace remained in use longest in England when it was used until 1990 by Capper Pass as the best choice for smelting low grade, complex tin concentrates - mainly because it could be operated continuously, did not require hand working of the charge and could handle large quantities of slag easily. It was used to produce a tin/lead alloy from which tin was obtained by electrorefining. The blast furnace was last used for smelting to tin metal also by Capper Pass in 1950 (Wright 1982).

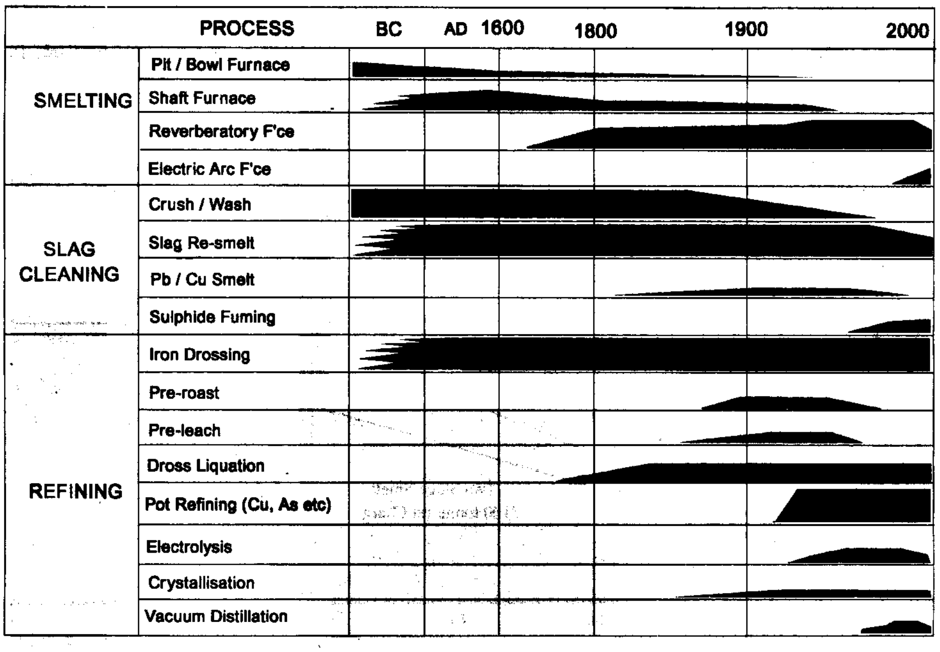

Fig. 3. Development of smelting and refining processes.

Reverberatory Furnaces

The main attraction of the reverberatory furnace is often given as its ability to use coal as a fuel rather than charcoal and although this was undoubtedly an advantage it may not have been the essential reason for the change. Carew in 1602, writes:

> The East quarters of the Shire are not destitute of Copswoods, nor they of (almost) on intolerable price: but in most of the West, either by nature hath denyed that commodity, or want of good husbandry lost it. Their few parcels yet preserved, are principally imployed to coaling, for blowing of Tynne. This lacke they supply, either by Stone cole, fetched out of Wales, or by dryed Turfes, some of which are also converted into coale, to serve the Tynners turne.

This clearly shows that a century before the introduction of the reverberatory furnace there was a shortage of wood in Cornwall but that the sort of wood used for charcoal was obtainable and that alternatives such as coal or peat coke were being imported or produced within the county. In 1778, Pryce was adamant that the one of the clear advantages of the reverberatory furnace was its ability to use Welsh coal; nevertheless, blast furnaces continued to be used in Cornwall for 150 years after its introduction. One must conclude that fuel was an important factor in the acceptance of the reverberatory furnace but was not an essential.

The advantage that the reverberatory furnace did not require a supply of water to drive bellows does not seem to have been a determining factor in Cornwall.

When the reverberatory furnace was introduced at the beginning of the 18th century, Cornish miners were increasingly working lode deposits rather than alluvial placers. Here cassiterite was firmly bound in a rock matrix and it was more difficult to produce the clean high grade concentrates needed for the blast furnace. This could be done at the expense of producing smaller particles which were easily lost in tailings and as blast furnace soot. From a metallurgical point of view, the reverberatory furnace allowed the treatment of finely ground, medium to high grade concentrates (55% Sn upwards) in a way that the short blast furnace could not and it would perform at least as well on high grade materials. It possessed the overwhelming advantage that small amounts of arsenic and sulphur, which were more prevalent in mined ores, were removed by oxidation as the charge heated up and in severe cases the furnace could be used as a roaster.

Lydall's patent of 1702 (Barton 1971)) for the smelting of tin in reverberatory furnaces is interesting. It claims the advantages of smelting 'without the Help of Bellows' and

> ..by meanes of some peculiar Fluxes, whereby not only a greater produce of White Tinn is made out of Black Tinn and with less charge than usual, but also the Consumption of Wood and Charcoal which in Smelting and Melting Black Tinn into White Tinn hath been very great will thereby be much lessened, to the great benefitt of the Publick

Strangely the patent does not mention coal or culm (the reducing agent) and it is left to a subsequent patent granted in 1705 to claim:

> A new Art, Method or Invention, of separating and refining Gold and Silver from Tynn by Precipitation, and likewise for melting and smelting Black Tinn Oar into good merchantable White Tynn, with Culm and Sea Coal, in a Blast Furnace called Ignifurens, whereby much more Gold and Silver may be obtained and more White Tinn melted from the Oar, and much cheaper than can be produced by any method now in use to the great enriching of our Countyes of Devon and Cornwall .....'.

Why the patents were phrased in this way is unclear and there are several possible reasons which will not be speculated upon here.

In 1699 Lydall was the expert at the Neath copper works and had close contacts with the Flint lead works; both operations were using the reverberatory furnace and were roasting and smelting both lead and copper ores. Lydall went into partnership with Francis Moult and Sir Richard Hoare and set up furnaces at Newham (Barton 1971) for the smelting of tin. Around 1704 John Heyden, the Newham assaymaster, developed the use of cast iron as an additive for the smelting of tin. This caused ructions. Lydall left the partnership, of which he had only a small holding, because he disagreed with the practice of adulterating tin with a base metal and Moult & Co. became the defendants in a court case in which they were accused of producing inferior tin. The implication was that the cast iron diluted the tin and produced a metal which passed the coinage test but in all other respects it was sub-standard when compared with tin produced by blowing. Heyden's success is demonstrated by depositions on oath stating how Moult and Heyden had used ores from the dead heaps at the notorious Relistian mine, which 'had little or noe tinn in it and being melted by its selfe produced a hard brittle stinking metall and minerall....' and that they were also using 'vast quantities of skimpings and flying top dross'. The technical aspects of the case

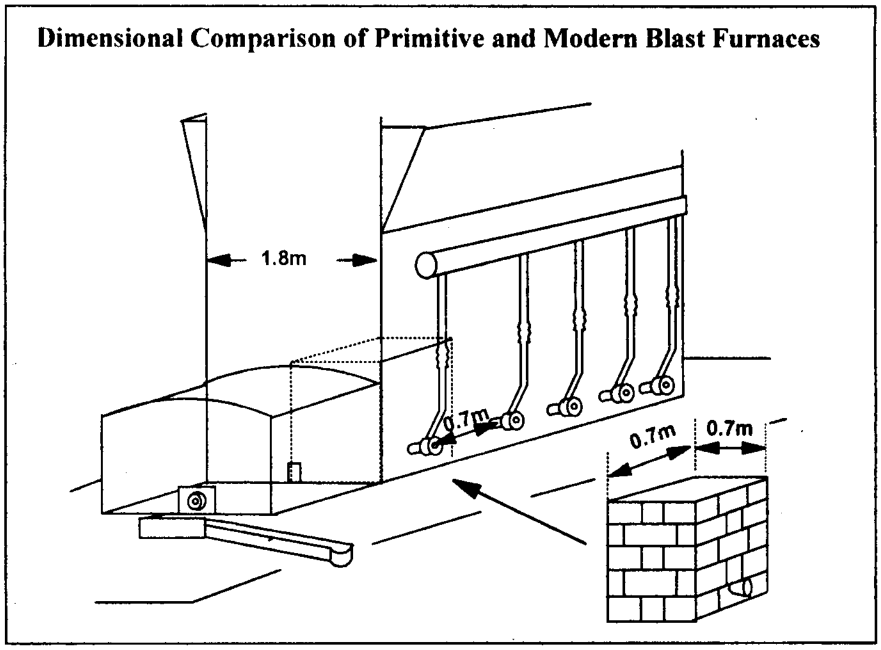

Fig. 4. Primitive and modern blast furnaces.

were solved by arbitration on the metal quality by the Royal Mint (which action also challenged the authority of the Stannary Court and caused further dissatisfaction). By the time the Royal Mint come to a conclusion in 1708, the Newham works had perfected the refining process for iron removal and the arbitrator declared that no difference could be found between blown and smelted tin.

The metallurgy of using cast iron additions is interesting in that one might expect this to be the last thing that should be added to tin. There are in fact advantages:

1. Cornish ores are typically alumino-silicates and low in bases such as Ca and Fe, unless iron is present as a sulphide. Tin forms a stannous silicate slag, which is one of the principal sources of loss. The addition of iron displaces tin from the silicate matrix; this is thermodynamically favoured and assists reduction to a low Sn slag:
   $SnSiO_3 + Fe = FeSiO_3 + Sn$.
2. Lime (usually added as chalk or limestone) is more effective than iron and is preferred as an additive, although it raises the melting point of the slag. Therefore, small additions of iron are sometimes made, with great care, to obtain a fusible slag (Strachan *et al* 1990) and to reduce tin losses.
3. When small amounts of iron are present with tin, below 800°C a range of intermetallic compounds Fe_2Sn, Fe_3Sn_2, FeSn and $FeSn_2$ precipitate (Wright 1966; Wright 1982; Mantell 1949). This is shown in the FeSn phase diagram Fig.5. If larger quantities of metallic iron persist then free Fe freezes above 800°C. As arsenic and iron form a compound, (Fe_2As in a matrix of Fe) there is a possibility for this to form, and for arsenic to be partially removed from the system above 800° C. This was used by 19th century whitemetal alloy smelters to remove arsenic, although it is generally ineffective as a means of completely removing arsenic. At Capper Pass, the ratio of As in iron to As in metal was approximately 9% to 1.5% for blast furnace solder and 25% to 1% with lead. In the high-grade smelter, the iron drosses produced on tapping the furnace contained arsenic but not those produced at lower temperatures.

In summary, therefore, it appears that the reverberatory was initially developed for tin smelting by Lydall as a logical extension of its use for lead and copper smelting. He sold it to Moult and partners simply as a means of obtaining tin at a lower cost than could be achieved by blowing - fuel was only one of the factors in this choice. Once it was put to work on routine smelting duties, its superior metallurgical capabilities became apparent and placed the Newham works in an extremely strong commercial position in that in addition to the lower unit costs, it could effectively treat dirty concentrates, which were cheaper to buy than conventional materials. At the same time, the Newham partners improved iron removal processes to produce a formidable combination which could not be challenged by the blowing furnace. The addition of cast iron seems to have been quickly discontinued for tin smelting but has been retained for solders and whitemetal residues until the late 20th century.

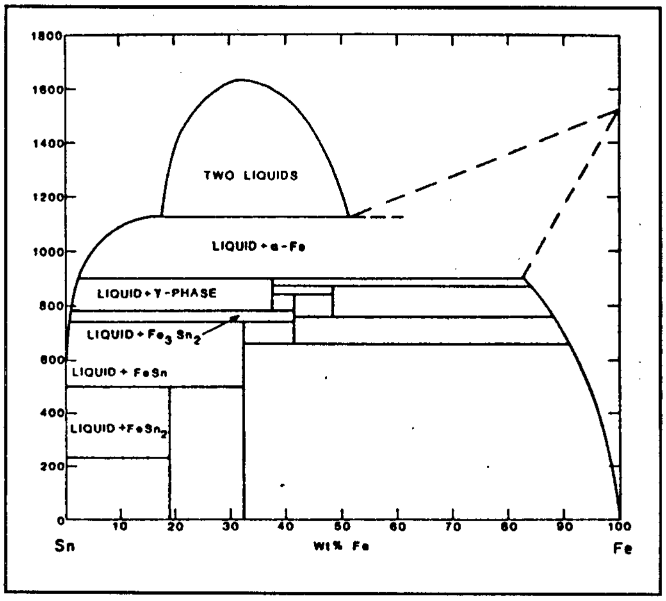

Fig. 5. The Sn-Fe phase diagram.

The reverberatory furnace and its near relative the rotary furnace has been the main workhorse for tin smelting at large works since its inception. The main improvements in its design have been in the 20th century and have included: replacement of stationary coal grates with pulverised coal or oil firing burners; heat recovery by means of brick 'chequers'; addition of fume arrestment devices; construction of purpose built furnaces for high temperature slag smelting.

The reverberatory furnace is currently under threat from the electric arc furnace (Strachan *et al* 1990) which has the advantage of lower off-gas volumes (and hence lower fume arrestment costs) and can achieve much higher operating temperatures (this ensures fluid slags under nearly all conditions and obviates the need for hand rabbling). High temperatures also permit very reducing conditions and because of this the electric furnace has been used for slag smelting at THAISARCO where it has been used to obtain a tin-free slag, high in Nb and Ta and undiluted by lime additions (Wright 1982).

IRON DROSSING OF CRUDE TIN

When tin is tapped from a furnace, the tapping run and pot becomes encrusted with a granular brown deposit with silvery bright crystals. The iron content of this dross can be up to 15% Fe and although the phase of interest is Fe_2Sn or Fe_3Sn_2, a large part of the dross is entrained tin metal (Fig.5). As the tapped tin cools, a dross rises to the surface which contains different tin/iron alloys of which FeSn is generally regarded as the dominant species, the dross at this point is very wet and typically only 5 %Fe (balance Sn). Below about 400°C, $FeSn_2$ is formed which is denser than tin and has to be gently oxidised to persuade it to rise to the surface. This is done in a number of ways including blowing with steam or air, vigorous stirring or pouring from a ladle (tossing); adding coal, green wood, or vegetables such as turnips or potatoes in an inverted vessel held at the bottom of the pot. Overzealous blowing etc results in the formation of tin oxide and does not seem to speed up the separation. Success seems to depend on allowing the dross to form first at the bottom of the pot and then to slowly persuade it to rise. No conclusive studies have been reported on the mechanisms for this part of the process although it is generally believed that it relies on the formation of a surface layer of oxide which prevents wetting of the particles of dross by molten tin. At this point the dross is commonly <1 %Fe. Overall, a combined dross of 10-15 %Fe (balance Sn) is obtained. with the aid of a metal centrifuge and up to 8 %Fe using only a perforated shovel. As can be seen from these figures, which are recollections from personal daily experience, the presence of small quantities of iron results in a massive circulating load of tin.

Agricola's furnace arrangement of an open forehearth with bottom tapping to a dipping pot, which was a hollow in the ground was conceptually similar to Cornish blowing furnaces with their float and stone holding mould. These would permit some separation of iron drosses but would not allow molten tin to be held for extended periods; it is likely that the eventual purchasers would unwittingly refine the metal further when they remelted it for use.

Liquation furnaces have been used increasingly to attempt to improve yields by separating tin from iron drosses. Although they were described by Agricola (1556) and were virtually identical to the saigerofen used for liquating copper/lead cakes, liquation does not appear to have been used for tin in England until after the introduction of the reverberatory furnace around 1704.

At some works, liquation would be carried out in the same furnace used for smelting. This would be charged with tin blocks, which were gradually heated and progressively poorer grades of tin sweated out. The furnace would be refilled a number of times. Finally the temperature would be raised and the final residue known as 'hardhead' tapped out and recycled to the smelting charge, stockpiled or sold to copper alloy or solder smelters.

IMPURITY REMOVAL

The impurity removal processes in Figs 3 and 10 are outside the scope of this paper as they can be considered to be quite separate from the smelting flowsheet or are relatively modern. The only one of these which is of interest in this particular context is that of arsenic and sulphur removal by roasting. Roasting kilns were in use in Cornwall in the later part of the 17th century (Anon 1671), several decades before the introduction of the reverberatory furnace.

At first sight there can be nothing simpler than heating arsenopyrite in a reverberatory furnace with the doors open and arsenic being removed as As_2O_3. The understanding of arsenic roasting today is not well documented and there are many contradictions in the literature. Wright revises his account (Wright 1966) considerably in his second volume (Wright 1982) on tin smelting. Normally carried out at 800°C, the roasting atmosphere must be controlled accurately if arsenic is to be removed. If carried out, as might be expected in an excess of air, arsenic is not volatilised and it has been presumed that this is because of the formation of stable ferric and ferrous arsenates and arsenites. Although there is little published work on the subject, those who have been faced with this problem have found that sulphur must be present to enable arsenic to volatilise as the sulphide which then burns to arsenious oxide when air is introduced in the offtake flues. The temperatures involved are much higher than is needed for volatilisation of As_2O_3 but necessary for the less volatile As_2S_3. The problem is hardly noticeable in a multi-deck roaster where fresh feed on the top is in contact with sulphurous gases with a reduced oxygen content coming from the lower decks. It may be less noticeable also when major amounts of arsenopyrite concentrates are roasted for making arsenic.

Earl (1983) suggests that early arsenic roasting might have been carried out under reducing conditions or at least in a deficiency of air. The subject is beyond the scope of adequate discussion on this paper but is mentioned here as a relevant aspect of tin processing and one which should receive further attention.

PROCESSES FOR SLAG CLEANING

Crushing and separation of tin prills

The recovery of metal prills from the scoria of pit furnaces is a natural and obvious part of the operation and must have been practised from prehistory. This has been passed on as the means of removing metal from the slags of small blast furnaces and is well-documented either directly (Agricola 1556) or by reference to the product 'pillion tin' (Beare 1586). The need to do this demonstrates the poor phase separation which is obtainable in an unenclosed forehearth or float and is one of the major disadvantages of small blastfurnaces when used for tin, lead or copper, particularly when they are worked with an open taphole. After crushing, entrained tin prills are unaffected or flattened and it was normal to remove these by hand-picking, sieving or ore dressing methods(the author's experience with a pilot-scale electric furnace with a 50-60 Kg charge has been that good separations were usually possible if metal and slag were tapped together and left to solidify in an ingot mould). Similarly, it is easily overcome in large furnaces where there is sufficient time for settling to take place.

Prill recovery seems to have fallen out of use in the early part of the 20th century.

Slag Resmelting

Resmelting of slags is probably as old a process as prill separation and is useful where the prills are present as finely dispersed particles and mechanical separation is difficult (Agricola 1556). It is also used where incompletely smelted materials are entrained in the slag. Although the aim is to reduce tin from the silicate slag matrix, there are limits to this in a short blast furnace, simply because an already-formed slag passes through so swiftly that there is little opportunity to reach a significantly higher temperature than the melting point. For this to be effective, slag smelting in blast furnaces is usually carried out with a higher fuel to charge ratio than for the primary smelt and with higher blowing rates.

Additions of lime will displace tin from slags very effectively and help by increasing the melting point of the slag and in reducing slag density and viscosity if correctly proportioned. However, because of the short residence time in the small blast furnace only small additions can be made and if overdone can cause the furnace to seize. Repeated resmelting also accumulates fuel ash constituents into the slag - these are usually high in sodium or potassium and lower the melting point quite significantly.

The reverberatory furnace, on the other hand, produces a slag which is fairly well equilibrated and repeated slag smelting under the same conditions is not generally effective. However, it can be operated up to any temperature which the furnace will withstand and is therefore used at up to 1400°C, often in specially designed furnaces.

Smelting slags with copper or lead materials to produce alloys

Very good extraction (down to below 0.5 %Sn) can be obtained when tin slags are smelted with copper or lead charges. This has been used as the basis for treating low-grade ores in the 20th century and as the means of extracting tin from the slags and fumes of other metal smelters. In the 19th and 20th centuries it was normal for manufacturers of type metals and copper alloys to purchase old Cornish tin and lead slags as a source of metal.

Other methods

The development of sulphide fuming processes during the mid-20th century, where molten slag is treated with pyrites above 1100°C, is now gaining acceptance with high and medium grade smelters.

OVERALL FLOWSHEETS FOR TIN SMELTING AND REFINING

Whereas the unit processes for smelting, refining and impurity removal have received considerable discussion by historians, the overall process flowsheet has not - and yet the treatment of slags, drosses and other metallurgical intermediates is fundamental to the economics of the industry. By looking at flowsheets we can understand why, even today, tin is sold principally by brand name to individual users and why most producers make a wide variety of brands.

Metallurgical flowsheets are usually influenced by two extremes:

(a) - recycling of intermediates back to a previous stage is avoided out and separations of dissimilar materials are made wherever possible. This minimises the rework of recycling burden but invariably results in the smelter having to process many minor intermediates towards the back end of the circuit and usually generates a range of metal products having different purities.

(b) - recycling of intermediates back to an earlier stage of the process to simplify the process and to generate saleable metal and discardable slag with as few stages as possible.

Tin smelting flowsheets have generally progressed from style (a) to (b) over three centuries as follows. The following do not represent universal practice by any means; local variations, anachronistic methods etc certainly existed. Minor arisings such as fume, casting drosses etc are not shown but their treatment routes are normally straightforward. Nevertheless, there has been a general shift in flowsheet strategy which is reflected in the following examples.

Early Blast Furnace Circuits

Perhaps the best place to start are the descriptions of 19th century 'Chinese' practice in Malaysia and Indonesia collected by Louis (1911). Slags were repeatedly stamped and resmelted in short blast furnaces of similar dimensions to the Cornish blowing furnace, burning charcoal fuel and almost certainly treating similar grades of concentrates. These accounts are well-documented, practices were duplicated at widely separated operations and were clearly successful over a long period of time. The simplicity of the equipment permitted few variations. Fig.6 shows a typical flowsheet.

If we now look to the accounts of Beare from 1587 and Carew of 1602 there are few direct leads as to possible process flowsheets but we do know from Beare that different grades of tin were produced Even earlier in 1198, the royal decrees issued through William de Wrotham (Lewis 1908) show that two smeltings were carried out and that they were separately taxed at different rates. It is logical that these refer to smeltings of ore and slag although it is not clear if these were carried out by different parties. The 1671 account of the 'Inquisitive Person' (Anon 1671) and of Cotton in 1664 unquestionably refer to stamping and extraction of prills together with resmelting of slags. Finished metal appears to have been dipped straight from the float and heated refining kettles were not in general use in the mid-17th century. At best, some fast and furious degree of refining could possibly have been carried out using an unheated intermediate stone mould. Archaeological evidence will help elucidate this view.

If these unit processes are put together one arrives, almost inevitably at a close approximation to the Chinese circuit of Fig. 6 but with some differences: Beare tells us that prills were sold as a separate grade ('Pillion' tin) and that metal was also derived from slag ('Sinder Tin'). 'Hard Tin' is a little more difficult to place but most probably it refers to metal contaminated by small amounts of arsenic or copper which was expected by the tin blower to fail the test at the coinage. A proposed circuit is shown in Fig. 7.

Eighteenth Century Cornish Circuit

The early Cornish reverberatory flowsheet which can be derived from Pryce (13) is little different from that of Figs.6 and 7. Slag cleaning continued to depend on stamping and sieving or picking followed by stamping and washing (Fig. 8). A second slag smelt is not described and the reasons for this are logical. The silicate part of the slag was in complete

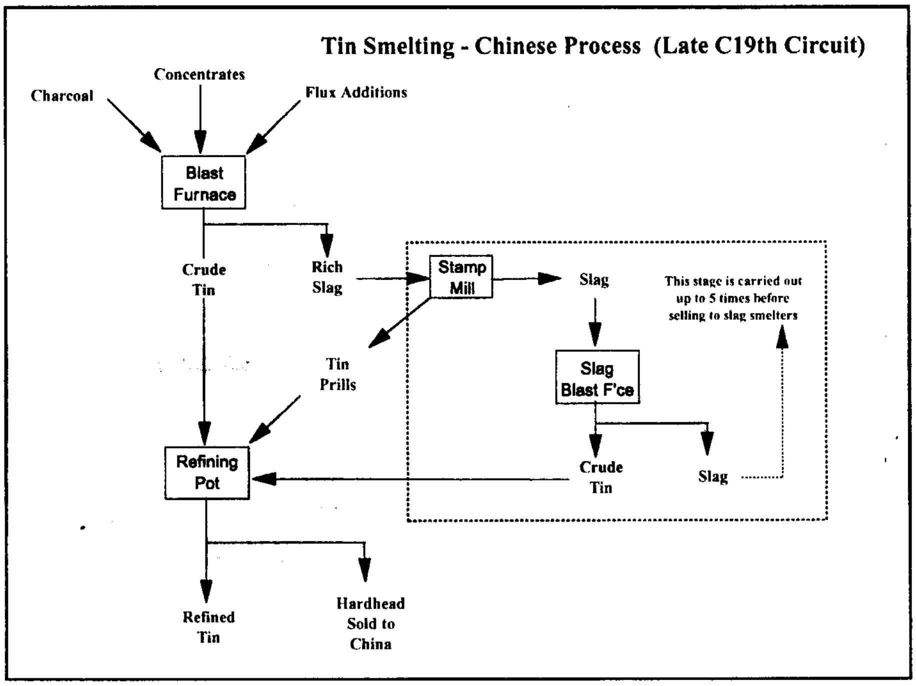

Fig 6. Flowsheet - Chinese Process, (late 19th c.).

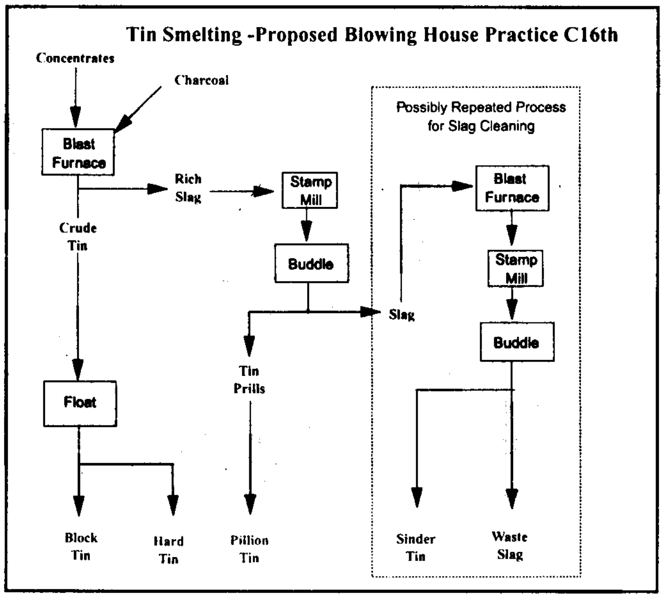

Fig 7. Flowsheet - 16th c. blowing house practice.

equilibrium with tin at the time of the ore smelt. Once prill tin had been removed, the remaining tin held within the slag matrix could not be removed in a reverberatory furnace, unless a higher temperature or additives were used. The Cornish fire assay would show the slag to be clean, simply because it was incapable of determining tin at the levels found in the silicate part of the slag. A major difference from the blowing house regime of Fig. 7 (Pryce 1778) was that tin was allowed to solidify before being treated in a liquation furnace (which was often a normal smelting reverberatory). Pryce gives no description of refining pots or kettles but by this time there were kettles and attendants known as 'kettlers' employed in the industry (Barton 1971). Hatchett writing in 1796 refers to tin from reverberatory furnaces at St Austell being run into an iron pot but there is no mention of any refining being carried out. It was afterwards cast into stone moulds and was refined by remelting. However, he does mention the use of refining pots in conjunction with a blowing furnace. Liquation residues could be expected to be returned to the smelting furnace where the iron content of the hardhead would act as a flux for new concentrates.

The flowsheet shown here depicts only one grade of tin. The trials on the first reverberatory tin (Barton 1971)) at the start of the 18th century by the Royal Mint (described above) suggest that only one type was made and if iron removal was carried out properly this would be possible. Harder tin from the bottom of the casting pot could easily have been allowed to solidify and could have been returned to the liquation furnace.

The use of cast iron as practised at Newham for tin smelting (Barton 1971) does not seem to have become general and it is probable that the need for this was obviated by the more widespread roasting of mined ores to remove arsenic.

Nineteenth Century Cornish Circuit

The flowsheet used at the Penzance works in the late 19th century (Fig. 9) is reported by Louis (1911) and can be found in other books (Thibault 1908; Mantell 1949). The demands of large scale production become apparent in the design of this circuit. Waste slag was obtained as directly as possible with the minimum of crushing or smelting and as much entrained tin as possible was extracted from hardhead, which was sold or recycled to an earlier smelt. Otherwise the circuit is conceptually similar to that of Pryce.

During smelting, the charge was repeatedly rabbled to allow tin to settle from the upper slags in the reverberatory furnace. When the smelt finished, the 'top slag', which was 60% of the total, was drawn off and discarded with no further treatment. 'Middle slag was drawn off, stamped and then discarded. The remaining 'bottom slag' was resmelted together with the prills from the 'middle slag'. Bottom slag would have been at the metal/slag interface and would have had metallic tin, iron and possibly matte or speiss in it. Molten slag which ran out into the float with tin was known as 'glass' and was also resmelted. Concentrates were a mixture of Cornish (62 - 65 %Sn) and Bolivian (up to 72 %Sn). Waste slag was said to contain 2 - 5 %Sn.

Two-Stage Smelting Circuit

In the late 19th and 20th centuries, the so-called 'two-stage' smelting process for tin became the standard approach for reverberatory smelting (Fig. 10). It is at the heart of the

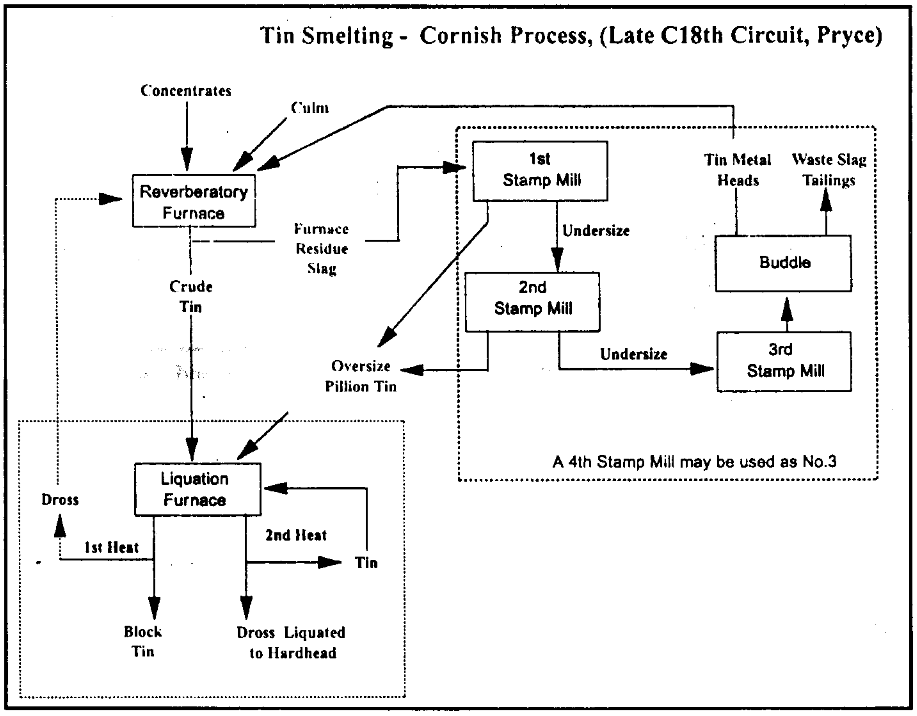

Fig 8. Flowsheet - Cornish process (late 18th c. circuit, Pryce).

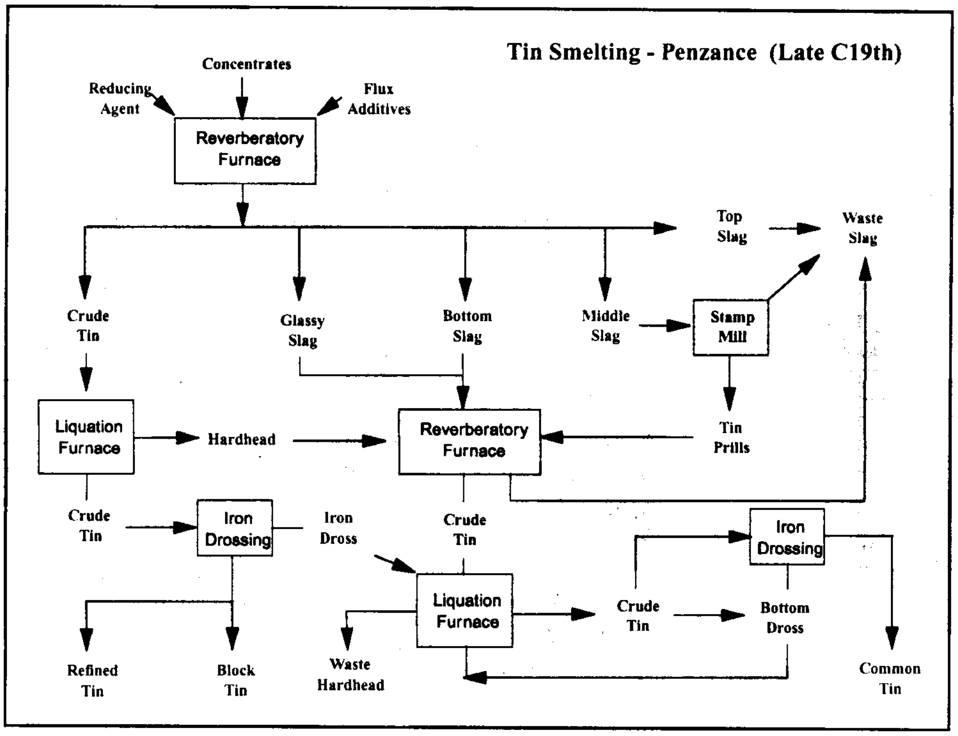

Fig 9. Flowsheet - Penzance Works (late 19th c.)

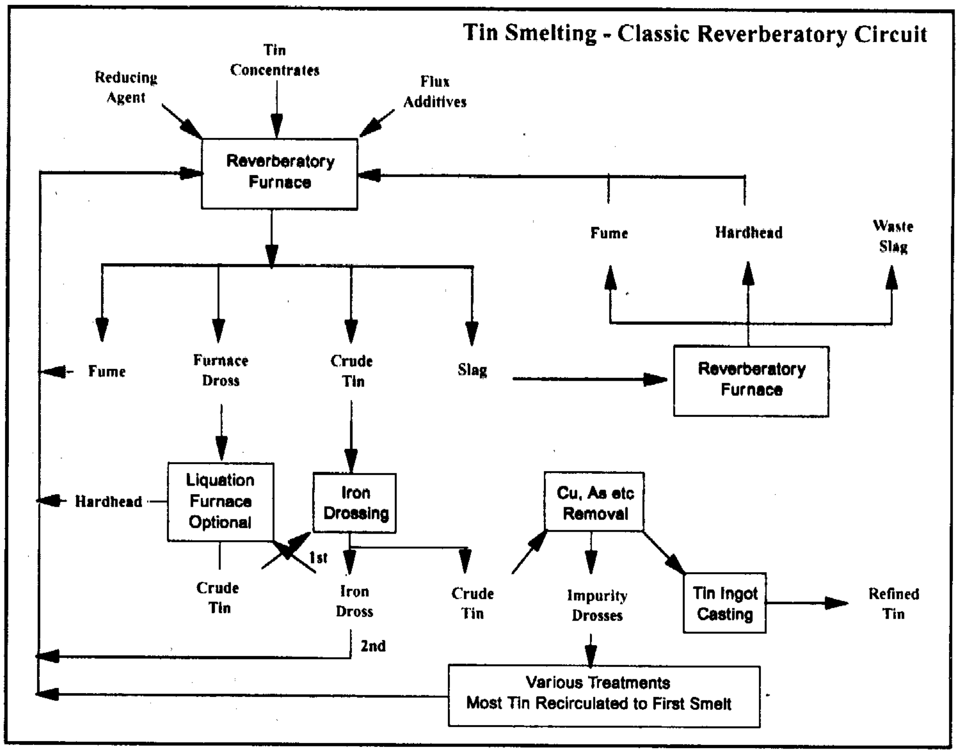

Fig 10. Flowsheet - Classic reverberatory furnace.

circuits of many works (Mantell 1949) and has been described and mathematically modelled by Wright (1982). A later 'three stage' process has since been used at Williams Harvey at Kirkby and in south east Asia and is more tolerant of recycling iron from lower grades of concentrate (>45 - 55 %Sn).

The two-stage process is simple in concept:

> ***Ore smelt*** - concentrates, fume, iron drosses and hardhead are smelted at about 1200°C to produce crude tin metal with about 2 %Fe and a fluid slag containing up to 10 - 20 %Sn.
>
> ***Slag smelt*** - slag and usually additional lime are smelted at high temperatures up to 1400°C to hardhead containing 20 - 55% Sn and 30 - 55 %Fe, together with a waste slag of 1 - 2 %Sn.

Waste slags of 0.5 %Sn can be made by intensive smelting with high lime additions but this produces more iron, which in turn generates a recycling load of dross which cannot be accommodated unless very high grade concentrates are being processed. Metal from the first smelt is refined in pots to remove Fe, Cu, As and traces of Sb or Pb - the latter being removed inefficiently. Iron and other drosses are sweated or liquated to release entrained tin, which is by far the main constituent and then processed to eliminate the impurities and recover more tin. The process is limited by the recycling load of iron which becomes more important with lower ore grades.

The two-stage process relies on the first smelt producing a fluid slag, with a controlled tin content, at a relatively low temperature. This allows clean metal separation from slag and overcomes the need for crushing and prill removal. However, it needs either a very consistent source of ore or good slag assaying methods, not only for Sn but also Fe, SiO_2 and CaO, to ensure adequate slag control. The development of better refractories and fume arrestment has enabled more forcing conditions to be used for the slag smelt. The adoption of wet analytical methods and to a lesser extent the cyanide fire assay, have given a true representation of the tin content of waste slags.

It will be noted that flowsheet of the Penzance works in Fig. 9 does not rely on a fluid slag and leads to higher losses. However, because the slag is not fully equilibrated with the metal it is very probable that the amount of iron in tin would be less than with the two-stage process. The two-stage process also eliminates much of the hot arduous work entailed in drawing solid slags, particularly from the furnace bottom.

CONCLUSION

In the twenty years before 1992, virtually the whole of the tin smelting industry in Western Europe and North America closed down. This included two smelters each in the UK, Spain, Germany and one each in Bolivia, Denmark and the USA. With exceptions in Spain and the UK, mining for tin is no longer carried out and a centuries old tradition has more or less come to an end.

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