J Mater Sci (2009) 44:2181–2191
DOI 10.1007/s10853-008-2942-1

FESTSCHRIFT IN HONOUR OF PROF T R ANANTHARAMAN ON THE OCCASION OF HIS 80TH BIRTHDAY

The origins and inspirations of zinc smelting

Paul Terence Craddock

Received: 18 April 2008 / Accepted: 8 August 2008 / Published online: 20 September 2008

Abstract The smelting of zinc was one of the most challenging technologies of the pre-modern world; indeed in the application of scientific techniques to industrial processes it anticipated modern industrial practice. Very different approaches to the problem evolved in different parts of the world. As the process required the condensation of the metal from a vapour, it is likely that some of the then current distillation practices might have provided an inspiration for the process adopted. Specifically, the techniques employed for the production of mercury may also have provided methodologies that could be adapted.

Introduction

The production of metallic zinc must represent one of the most advanced technical processes of the pre-modern world. Indeed the development of these processes can be seen as forming a continuous link with the Industrial Revolution which is regarded rather narrowly by some as being exclusively a European-North American phenomenon of the 18th and 19th centuries AD.

Around the world very different systems were evolved to reduce the zinc ore and then to condense and collect the zinc vapour so produced [1]. This article will consider the systems that evolved in China, India and Europe. In each region it is likely that brass, the alloy of copper and zinc, was already being made by the direct process, reacting zinc ore with copper and charcoal in a closed crucible. In the ancient Near and Middle East the smelting of argentiferous lead zinc ores in conventional shaft furnaces inevitably smelted the zinc component as a vapour that promptly oxidised in the furnace flue to give dense white clouds of zinc oxide (hence the Old Persian and Sanskrit term *tūtīyā*, literally smoke, for the zinc oxide used to make brass). It could also be used medicinally as a salve, the basis of the familiar calamine lotion, and in the first century BC the Greek pharmaceutical writer, Dioscorides, described various methods for condensing some of the zinc oxide so formed on iron bars or on the walls of chambers set above the furnaces (Fig. 1) [2]. A thousand years later Islamic writers described complex arrangements of bars set above the furnaces where the zinc ores were smelted specifically to recover the *tūtīyā* [3]. There must have been a very low recovery rate with most of the zinc oxide being lost to the atmosphere. Zinc oxide was also collected from the furnace flues at the silver/lead mines such as Rammelsberg, near Goslar in central Germany in Post Medieval times (Fig. 2). Inevitably a little of the zinc condensed as droplets of metallic zinc within the sublimate. That this metal could be added to copper to make brass was recognised over 2,000 years in the well-known description recorded by the Greek geographer, Strabo [4], writing about the strange metal that dripped down when the lead–zinc ores were smelted at the silver mines near Andeira in present day north-west Turkey [5]. At Rammelsberg the deliberate formation of zinc metal by this method was being encouraged by setting cold chambers in the sides of the furnace flues, although production only amounted to a few hundred kilograms per year [6]. However, much of the zinc was still being lost and the realisation must have been common amongst brass makers everywhere that if a way could be found to condense the vapour then this

P. T. Craddock (✉)
The British Museum, London WC1 3DG, UK
e-mail: pcraddock@thebritishmuseum.ac.uk

Fig. 1 Vaulted chamber built over silver smelting furnaces to collect the zinc oxide. From [24]

Fig. 2 Workers scrapping zinc oxide off the walls of the silver/lead furnaces at Rammelsberg in the 16th century. From [25]

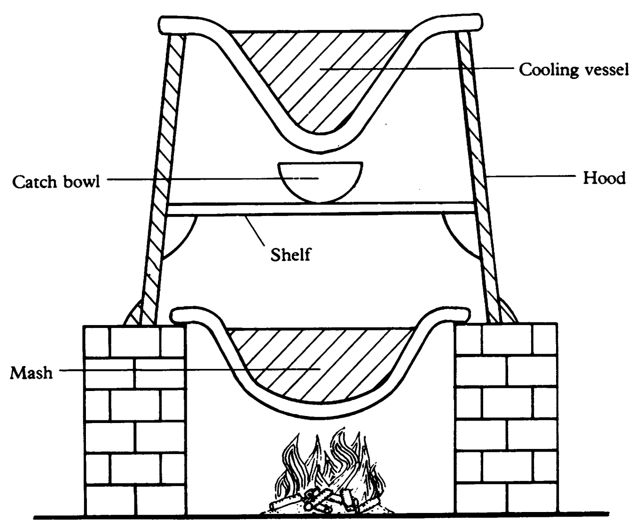

Fig. 3 Mongolian still with internal condenser. From [7]

would be a more efficient use of the zinc ore as well as producing a better brass.

The problems confronted in zinc smelting are three-fold. A great deal of energy is required to reduce the ores to metal. The zinc is produced as a vapour with a boiling point of 907 °C (although in practice the vapour has to be cooled to below 600 °C if it is to be quickly condensed, leaving only quite a narrow temperature range between the condensing and 420 °C solidification temperatures). Thirdly, this vapour is very reactive, being intensely reducing, such that an overpressure of carbon monoxide is necessary throughout the system. In each of the three regions to be considered it seems that the model for the condensation of the zinc vapour was based on the existing systems for the distillation of aqueous media, or more specifically mercury, suitably adapted to meet the much more challenging conditions required to smelt zinc.

China

In the Far East the usual method of distillation has the vapour condensing and collected inside the distillation vessel itself (Fig. 3), a system also known as the Mongolian still [7]. With aqueous media or vegetable oils the vapour condensed on the underside of a bowl of cold water placed on top of the retort. The internal condenser process was also used for the production of mercury. The internal condenser process was also used for the production of mercury [8]. When adapted for the production of zinc the top of the retort protruded from the furnace and the zinc condensed against the loose-fitting lid and dripped back down into the receiving vessel beneath (Fig. 4). The smelting technology that began some 500 years ago evolved through the centuries and was still functioning at the end of the 20th century [9]. The usual zinc ore used in China is smithsonite, hydrated zinc carbonate, and is found in the karst limestone hills of western central China where the present provinces of Yunnan, Guizhou and Sichuan meet.

Other metals, notably copper, also occur in the vicinity and much of China's *cash* coinage was produced here. Zhou [10] has suggested that the production of brass by the direct method for coin production was rapidly expanding into a large-scale industry about 500 years ago and the development of the production of metallic zinc, which was used almost exclusively for brass making, should be seen as a progression in the brass-making technology.

The ceramic retorts were charged with small lumps of ore and briquettes of the special low-sulphur coal that occurs in the region. The collecting dish was put in place but the condenser lid left off and the furnace was fired for some hours to calcine the ore. The lid was then put in place, the temperature of the furnace was raised and the smelting commenced, the process running for between 12 and 18 h, the whole process taking about a day.

From the start, it seems that many retorts were fired together and there is a well-known illustrated description given in the *T'ien-Kung K'ai-Wu* published in 1637 AD [11]. The well-known description and the illustration (Fig. 5) suggest that the retorts were fired in a conical pile, but this would not work, the lower parts of each retort has to be hot and upper part cool, something that could not occur in the arrangement shown in Fig. 4. It is possible that the original description and illustration was misunderstood by the compilers working thousands of kilometre distant in Peking and what was intended was a perspective view of the retorts all standing at the same level as found in the excavated and present day furnaces. The process was already being carried out some 500 years ago at Miaobeihou in Yangliusi village, Fengdu County in Chonqing, and at

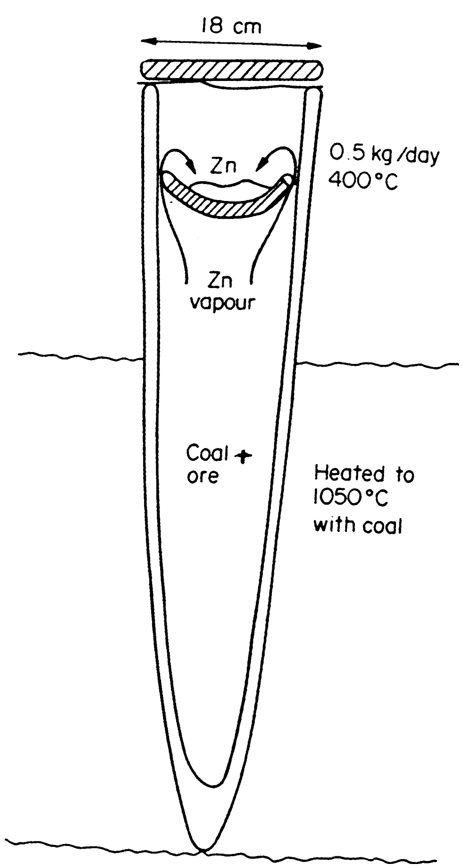

Fig. 4 Section through a zinc-smelting retort. From [26]

Fig. 5 Zinc smelting furnace from the *T'ien-Kung K'ai-Wu* of 1637. From [11]

Fig. 6 Remains of a 16th century horse trough type furnace. cf Fig. 7. From [12]

other sites along the Yangtze River. Recent excavations [12] have revealed the remains of furnaces showing they were similar to those used until the recent past (Fig. 6). Up until the 1970s, the furnace comprised a large rectangular trough, known as the horse trough furnace, with a series of 12 raised clay bars across the furnace bottom on each of which stood 3 retorts, making a total of 36 retorts per furnace (Figs. 7 and 8) [13]. Ordinary coal was then stacked around the retorts and then sealed at the top with a mixture of clay and coal dust, with the tops of the retorts protruding through.

It is rare for sophisticated local technologies to survive in the face of European imports or more advanced technologies (cf the fate of the Indian zinc smelting industry, described below), but due to the isolation of Chinese zinc-smelting industry and the peculiar circumstances of China's history through much of the 19th and 20th centuries, the traditional process thrived**,** even in Huize, Yunnan, where the traditional smelters were operating alongside the supposedly more efficient electrolytic plant established in the 1970s. Not only did the traditional process thrive but even evolved during the 1980s [9]. The principal change was to separate the fire from the retorts such that the flames were drawn through the retort chamber, which now contained between 80 and 100 retorts, and up into the chimney (Fig. 9). The usual arrangement was to have two units back to back with one side smelting whilst the other side was being loaded with retorts and charged (Fig. 10). In theory**,** at least this enabled more or less continuous production.

Fig. 7 Empty horse trough type furnace showing the bars on which the retorts will stand. cf Fig. 8. From [13]

Fig. 8 An abandoned horse trough furnace, probably of the 1980s, photographed in the 1990s, still containing its last load of retorts. From [9]

India

In India the distillation of zinc began about 1000 years ago utilising the traditional Indian distillation method of *adhaspatana yantram*, which is distillation by descending [14]. Some of the very early Indian descriptions of mercury production given in works such as the *Rasaratnakara* (7–8th century AD) or the *Rasahridya* (12th century AD)

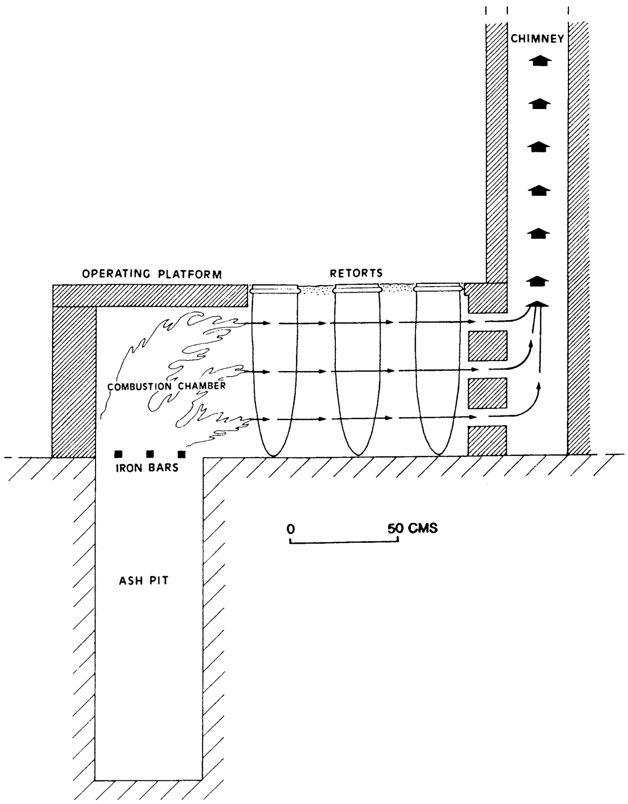

Fig. 9 Section through a 1990s zinc smelting furnace. From [9]

Fig. 10 A typical two-unit smelter near Huize in Yunnan. The fire boxes are on the outside of the retort chamber and with a central chimney. From [9]

describe how a pot containing the mercury ore is to be inverted over another pot containing water in which the descending mercury vapour condensed [15].

Zinc production in India was always centred on the mine of Zawar in the Aravalli Hills of Rajasthan in the north west of India. This was because uniquely at Zawar, the zinc ore could be separated by hand picking from the lead with which it is always associated. The industry began at Zawar in the second half of the first millennium BC, long before the production of metallic zinc, when the main product

Fig. 11 Fragment of a plate of zinc oxide. From [16]

seems to have been sublimated zinc oxide. The archaeological excavations of the early slag heaps at Zawar recovered fragments of flat plates of zinc oxide with adhering fragments of ceramic (Fig. 11), presumably from ceramic baffles or plates set over the flues in an arrangement similar to that shown in Fig. 1 [16]. The principal use of the zinc oxide so produced would have been in the production of brass, and at some time in the first millennium AD the process of condensing the zinc vapour was evolved, thereby cutting down on the losses. At Zawar, the zinc ore was sphalerite, zinc sulphide, and it would first have been necessary to roast this to eliminate the sulphur, and mounds of white roasting debris surround the main smelting areas at Zawar.

The roasted ore, still containing calcium and magnesium oxides and silica from the vein stuff, was made into small balls with sticky organic materials with charcoal and a little salt and placed in the clay retort. The contemporary descriptions of zinc production in the Indian scientific literature specify expensive materials such as lac, sugar and resins that appear in many other iatrochemical recipes [15], but these are laboratory preparations and it seems more likely that at an industrial unit such as Zawar the ubiquitous cow dung and charcoal would have sufficed. Examination of the material remaining inside some of the retorts reveals a sintered mass with an open structure. The small quantities of salt present had promoted the partial vitrification of the silica at temperatures in the region of 1100 °C. The reactions in the retorts were basically gaseous, with the generation of carbon monoxide gas to reduce the ore to zinc vapour and thus an open structure was essential. The open structure also allowed the necessary heat transfer through the body of the retort to proceed almost instantaneously by conduction and radiation rather than having to rely on the much slower conduction if the charge had been a solid mass. A conical clay condenser tube was then securely luted to the open end of the retort and a stick was inserted to stop the charge from falling out when inverted

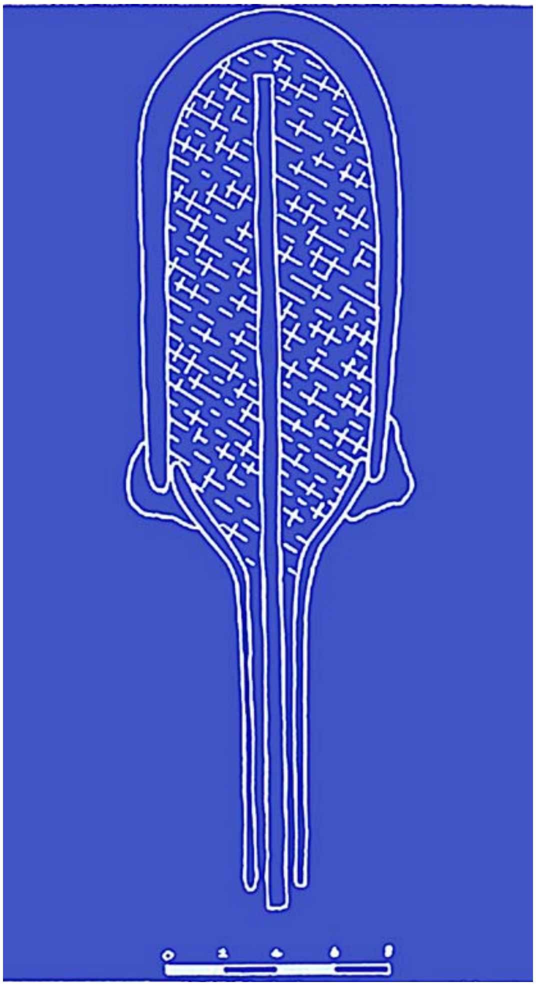

Fig. 12 Cross section through a zinc-smelting retort, 14–16th centuries, Zawar. From [14]

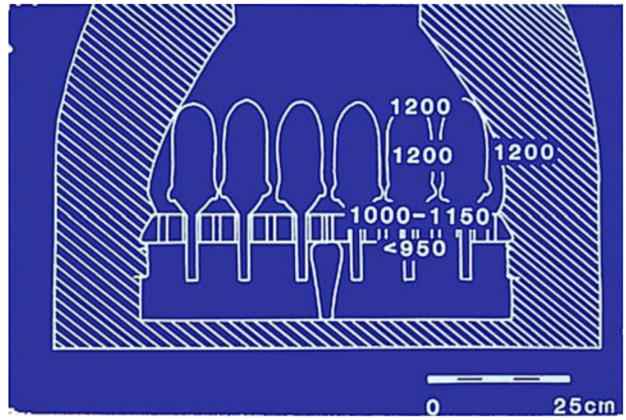

Fig. 13 Cross section across a *koshthi* zinc-smelting furnace showing the arrangement of the retorts, Zawar. From [14]

and to create a central channel down which the zinc vapour could pass (Fig. 12).

The furnace (*koshthi*) was divided into two parts, the upper furnace chamber in the shape of a truncated pyramid which was separated from the lower square cool chamber beneath by perforated bricks (Figs. 13 and 14). The form of the furnaces is not dissimilar to traditional pottery kilns, and possibly the kilns used to prepare brass by the direct method, except that in the latter the fire was in the lower chamber. The retorts were loaded into the upper chamber with their condensers sat in the large holes in the perforated bricks, and with their ends protruding into the cool chamber below. The retorts were set in a 6 × 6 array in the furnace. The furnaces were thus packed with retorts presenting a considerable surface area to the fire. As all the energy for the reduction taking place inside the retorts had to come from outside, the large surface area was desirable and enabled the process to proceed swiftly and uniformly through all the retorts. From a study of the penetration of the vitrification through the ceramic of the furnace lining,

Fig. 14 A typical bank of *koshthi* zinc smelting furnaces. From [14]

the smelting times at maximum temperature are estimated at between 3 and 5 h, which accords well with memories of the last surviving smelters when interviewed in the mid-19th century.

The furnaces themselves were grouped in blocks, the earlier (14–16th centuries AD) in blocks of seven and the later furnaces in blocks of three (16–19th centuries AD)

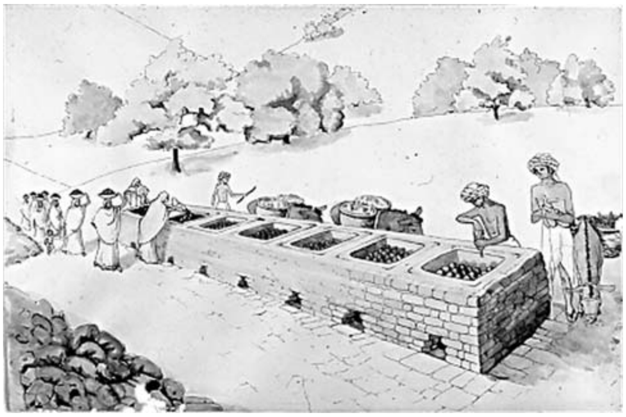

Fig. 15 Reconstruction of the charging of the furnaces with retorts as it would have taken place in the evening prior to overnight firing. From [14]

(Fig. 15). The process is estimated to have taken approximately 24 h and a furnace block would have produced between 50 and 100 kg per smelt. It is believed that many furnace blocks would have been in operation at any one time and thus production was on an industrial scale from the 14th to 18th centuries. During this period, the mines must have gone through many vicissitudes, the Mughal invasions etc. before ceasing production in the Maharatta wars in the early 19th century. Presumably work would have recommenced once peace was restored but by this time competition from imports, both from China, and increasingly from Europe, prevented the re-emergence of the traditional process. As with so many sophisticated technical processes, knowledge of it was soon lost, such that James Tod, author of the authorative *Annals and Antiquities of Rajputana*, published in 1830, could there describe the Zawar mines as having been worked for tin, less than 20 years after they had closed.

Europe

Once the sea routes to the East were opened up to European vessels in the Post-Medieval period, zinc was amongst the products brought back to Europe. As early as 1513, an Italian agent in Lisbon reported that a Portuguese ship loaded with 200 pieces of 'Indian tin' had just arrived from the East and that the English had better look to protect their tin trade. Outside of India, there was as yet no word for zinc, and in the lands bordering on the Indian Ocean, it was commonly referred to as Indian tin. Indian zinc continued to be imported into Europe, but was soon overtaken in international trade by Chinese zinc, usually transported in Dutch vessels [17]. In Europe, zinc commanded a high price for making top quality brass, and the very limited amount collected from the flues at Rammelsberg was used for this purpose, as already noted, mainly by the brass founders of Nürnberg.

The first company to produce zinc on an industrial scale was the long established brass manufactory run by William Champion at Bristol in England [18]. In that age of industrial espionage**,** Champion was extremely guarded in disclosing any details of the zinc smelting process, including how he had arrived at the process. It was described as being an independent discovery, but rumours of his having discussed the process with travellers from the East abound [19]. These stories are possible because the process is one of distillation by descending, very similar in principle to the Zawar process. The retorts sat in the upper furnace chamber with their condenser necks protruding through holes in the furnace floor into the cool chamber below (Fig. 16). However, there the similarities end. Champion's furnaces were based on the local Bristol glass furnaces and English brass-making furnaces [13, 20] and they contained six huge

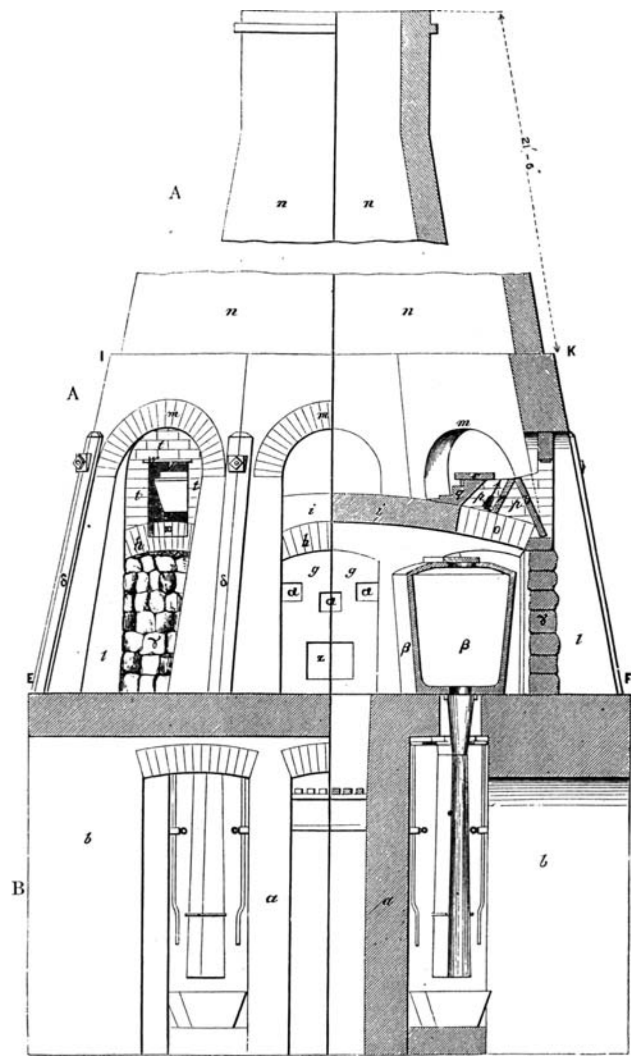

Fig. 16 Section drawing of a zinc smelting furnace of the type introduced by Wm. Champion. From [20]

retorts. The process worked, but not very successfully, and within 30 years Champion was bankrupt and his process never developed further and soon ceased altogether. Part of the problem was the large volume of the retorts that had to be heated. Unlike the Indian furnaces and retorts which had evolved over the centuries. The problem was that at Bristol there was no local tradition of high-temperature distillation processes that could have informed Champion and consequently his retorts only had a relatively small area exposed to the heat of the furnace. Brass makers from other parts of Europe were naturally intrigued and industrial spies descended on Bristol. They were able to report that Champion really was producing zinc but that the process was not very good. Some years later in Carinthia, on the Austro-Italian border, a downward distillation process was developed, but this time with hundreds of much smaller tubular retorts (Fig. 17). This arrangement was in fact much closer to the Indian process, but it is very unlikely that the Carinthian brass makers could have had any direct contact with Zawar. It is much more likely that the traditional central European process for the extraction and distillation of mercury was adapted for the production of zinc (Fig. 18), which at least in the arrangements of the retorts is superficially very similar to that at Zawar.

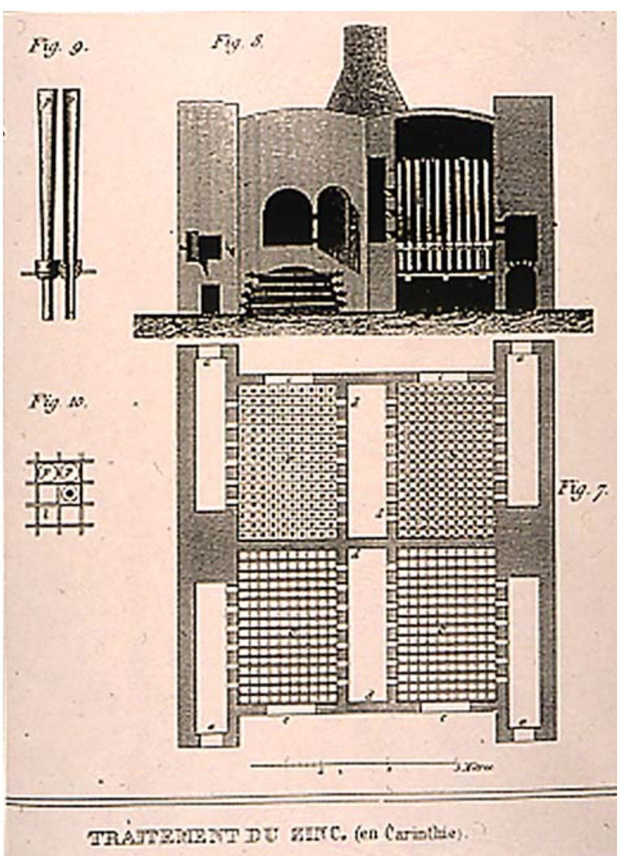

Fig. 17 Carinthian furnace. From [1]

Fig. 18 The production of mercury by downward distillation in the 16th century in central Europe. From [24]

In western Europe in the early 19th century**,** the horizontal retort process was developed to smelt the ores mined at the Vieile Montagne in Belgium by Jean-Jacques Dony (Fig. 19) [19, 20]. The origins of this process are uncertain, but over 1000 years before a very similar arrangement of retorts was employed for the distillation of rose water in Islamic Iberia (Fig. 20). Although the production of rose water continued for centuries, it would seem very difficult to make any connection between the two processes. Just possibly mercury distillation processes might provide a link.

The major mercury mine at Almadén, Spain, was, as the name suggests, worked by the Islamic occupiers of Iberia in the medieval period. The distillation process used in Islamic times is unknown but was probably a simple condensation inside a retort with a lid. However, by the 17th century a much more complex process known as the *Bustamante* or *aludel* process [21, 22] had been developed partly in the Spanish Americas and partly in Spain to meet the huge demand for mercury in the amalgamation process for the extraction of silver from its ores which had been developed in the 16th century [23]. The inclined retorts and aludels of the rose water process could have inspired the form of the Bustamante process. In the Bustamante furnaces illustrated in Fig. 21, the ores of mercury sulphides were placed on the shelf in the tall building on the left hand side and heated from beneath. The resulting mercury vapour could escape into the inclined lines of condensers (Figs. 21 and 22) made up of conjoined open pots known as aludels. Most of the mercury collected within them but

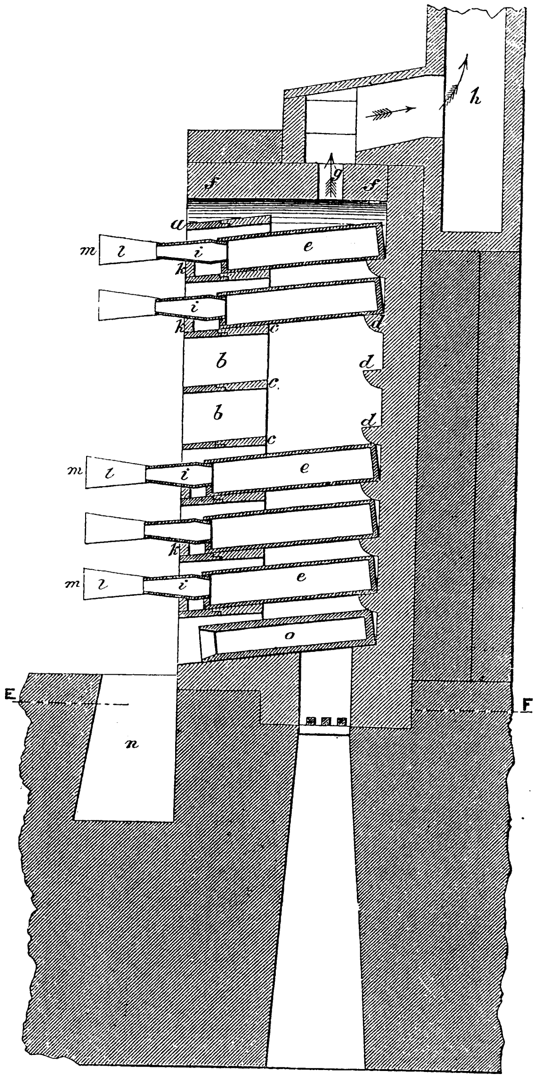

Fig. 19 Section through a horizontal retort furnace for the distillation of zinc. cf Fig. 20. From [20]

that which leaked from the joints would drain into the central gutter from which it could be collected. The fumes of sulphur and carbon dioxides, together with the small amounts of remaining mercury vapour, would ascend the aludels on the right hand side and into the tall chamber from which the fumes could exit from the top and the condensed mercury collect in the base.

The process was in use in South America and at Almadén through the 18th and 19th centuries and was reasonably well publicised in Diderot's *Encylopedie* etc. In addition, the Almadén mines had been carefully studied by the great Spanish scientist Augstín de Betancourt, who was to spend much of the late 18th and early 19th centuries travelling through Europe at just the time when Dony was developing his process with the encouragement of Napoleon. Thus it is possible that the lines of inclined horizontal condensers of the Bustamante process could have inspired


If it reaches the top of the cucurbit the righ
rose-water with all its phlegm is obtained. O
of phlegm. About one half or two-thirds of th

Fig. 13. A "mass-oven" for the distillation of rose-water, taken from an Arabian manuscript of unknown origine (Spanish?)

urbit should be distilled over. The furnace shal
om free of draught, not in an inner-court or the
omes the description of a smaller furnace and a w
ucurbits are heated directly by the fire, "mass-o

Fig. 20 Furnace for distilling rose water with horizontal retorts. cf Fig. 19. From [27]

the inclined horizontal retorts with their condenser prolongs of the Dony process.

Conclusion

The zinc distillation technology in India and China would seem to have been completely independent developments and in Europe, once the reality of the production of zinc on an industrial scale had been established, probably inspired by the Indian process, there were rapid developments of a variety of processes. The rising popularity of brass concentrated the search for a more efficient use of the sublimed zinc ore, leading to the production of the metal of metallic zinc as the feedstock in brass production. There was also the growing realisation that brass made by mixing the two metals was superior. The problems encountered establishing viable high-temperature distillation under very reducing conditions on an industrial scale were met by the brass makers across the Old World in different in a variety of ways. The form of the furnaces was variously based on pottery kilns, glass or brass making furnaces. The principle of the distillation technique

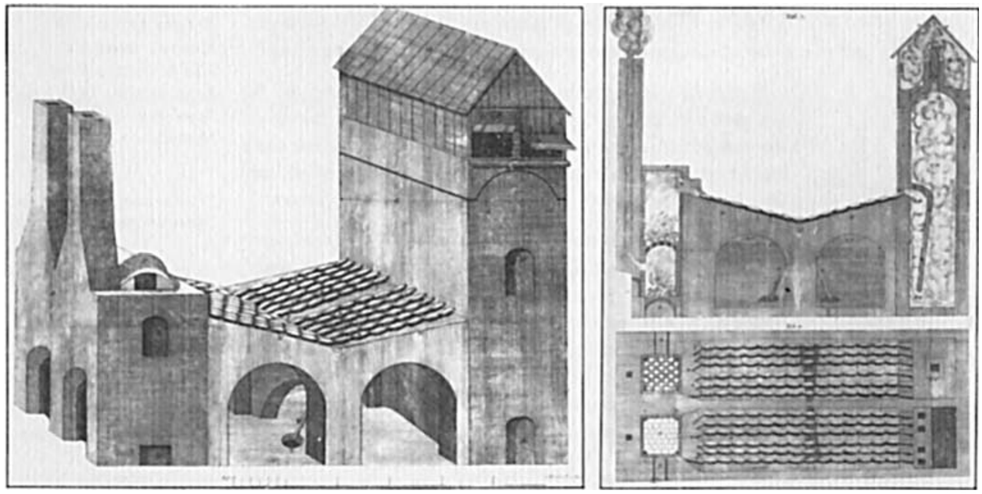

Fig. 21 Section through a Bustamante furnace at Almadén taken from the Dictionaire des Sciences, des Arts et des Métiers (Recueil des planches)

Fig. 22 View of the restored Bustamante furnace at Almadén showing the aludel condensers. From [22]

was usually adapted from the existing local prevalent distillation technology, especially for the production of mercury where such a technology existed.

However, there was a very considerable extension of the operating parameters necessary to produce metallic zinc and the diversity of solutions that were developed must command an admiration for the metal smelters across the world and through the ages.

References

1. Craddock PT (ed) (1998) 2,000 years of zinc and brass, 2nd edn. British Museum Occasional Paper 50, London
2. Gunther J (ed) (1959) The Greek herbal of Dioscorides. Hafner, New York, p 625
3. Craddock PT, La Niece S, Hook D (1998) In: Craddock PT (ed) (1998) 2,000 years of zinc and brass, 2nd edn. British Museum Occasional Paper 50, London
4. Jones RJ (trans) Strabo: Geography Book XIII 1:56. Loeb Classical Library, London
5. Craddock PT (1998) In: Craddock PT (ed) (1998) 2,000 years of zinc and brass, 2nd edn. British Museum Occasional Paper 50, London
6. Sisco AG, Smith CS (eds) (1951) Ercker: treatise on ores and assaying. University of Chicago Press, Chicago, pp 271–272
7. Needham J (1980) Science and civilisation in China V: chemistry and chemical technology IV: spagyrical discovery and invention: apparatus, theories and gifts. Cambridge University Press, Cambridge
8. Needham J (1980) Science and civilisation in China V: chemistry and chemical technology IV: spagyrical discovery and invention: apparatus, theories and gifts. Cambridge University Press, Cambridge, pp 77–78
9. Craddock PT, Zhou W (2003) In: Craddock PT, Lang J (eds) Mining and metal production through the ages. BMP, London
10. Zhou W (2007). In: La Niece S, Hook D, Craddock PT (eds) Metals and mines: studies in archaeometalurgy. Archetype Books, London
11. Zen Sun E-T, Sun S-C (trans and eds) (1966) T'ien-Kung K'ai-Wu: Chinese technology in the 17th century. Pennsylvania State University, Philadelphia
12. Liu H, Chen L, Bao W et al (2007) In: La Niece S, Hook D, Craddock PT (eds) Metals and mines: studies in archaeometalurgy. Archetype Books, London
13. Li X (1998) In: Craddock PT (ed) (1998) 2,000 years of zinc and brass, 2nd edn. British Museum Occasional Paper 50, London
14. Craddock PT, Freestone IC, Middleton AP, Gurjar LK, Willies L (1998) In: Craddock PT (ed) (1998) 2,000 years of zinc and brass, 2nd edn. British Museum Occasional Paper 50, London
15. Rây P (1956) History of chemistry in ancient and medieval India. Indian Chemical Society, Calcutta
16. Craddock PT, Eckstein K (2003) In: Craddock PT, Lang J (eds) Mining and metal production through the ages. BMP, London
17. Craddock PT, Hook DR (1997) In: Redknap M, Gaimster D (eds) Artefacts from wrecks. Oxbow Books, Oxford
18. Day J (1973) Bristol Brass. David and Charles, Newton Abbot
19. Day J (1991) In: Day J, Tylecote RF (eds) The industrial revolution in metals. Institute of Metals, London
20. Percy J (1861) Metallurgy. John Murray, London
21. Hauptmann A, Slotta R (1979) Anschnitt 2–3:81
22. Hernández A (1995) Las minas de Almadén. Editado por Minas de Almadén y Arrayanes, Madrid
23. Bargalló M (1969) La amalgamacion de los minerals de platta en Hispanoamerica Colonial. Compañia Fundidora et Fierro y Acero de Monterrey, Mexico City

24. Hoover HC, Hoover LH (trans and eds) (1912) Agricola: De Re Metallica. The Mining Magazine, London
25. Sisco AG, Smith CS (trans and eds) (1951) Lazurus Ercker: treatise on ores and assaying. University of Chicago Press, Chicago
26. Tylecote RF (1983) Metall Mater Technol 15(9):435
27. Forbes RJ (1948) A short history of the art of distillation. Brill, Leiden