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Brass, Zinc and the Beginnings of Chemical Industry

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Abstract

There have recently been a few major publications on the early history of brass and zinc. These have presented major new information on the history, technology and economic impact of the new metal, zinc. Based on these papers an effort is made here to provide an overview of the principal developments from the earliest times up until the rise of the European industry in the early 19th century. In both India and in China a striking feature of the production of zinc was the rise of a real chemical industry based on scientific laboratory practice, long before such developments began in Europe.

Key words: Brass, Chemical Industry, Distillation, Innovation, Process, Science, Trade, Zinc

1. Introduction

The most common copper alloy throughout the Old World for the last 500 years has been brass, the alloy of copper and zinc. Through the last 200 years zinc has become one of the most familiar and useful of materials, in its own right, as a protective cladding (galvanising), as well as in the oxidised forms, either zinc oxide as the zinc white pigment, or the carbonate as an ointment (calamine lotion).

Zinc ores are widely distributed, often occurring with other metals, such as lead and silver, yet it was one of the last major metals to be produced. The reason for this was the great difficulty in smelting the ores in a conventional furnace, which instead of producing a molten ingot in the furnace hearth instead produced a cloud of highly reactive vapour above the furnace.

Occasional finds of early copper alloys containing zinc have led to speculation as how they came about, and by the first millennium BCE there are the first textual references to a special alloy that could be brass. By the end of the millennium there are occasional references both in the Hellenistic World and in India to a metal that most logically should be interpreted as being zinc itself. In the first millennium CE in India there are detailed instructions given in the works of the iatrochemists for the laboratory preparation for the production of zinc by high temperature distillation. Sometime about 1,000 years ago these purely scientific procedures began to be developed into commercial processes for the production of zinc on an industrial scale. This took place at Zawar, Rajasthan, and as is now clear, at one other location, at least, in North West India (Fig.1).

Somewhat later the development of the production of zinc on an industrial scale also began in China, but using a totally different distillation technique.

Over the past few decades the story of emergence of zinc as a major metal globally has been the subject of major studies, including historic sources, scientific examination and above all, by archaeological excavation. This work has recently been published in a number of

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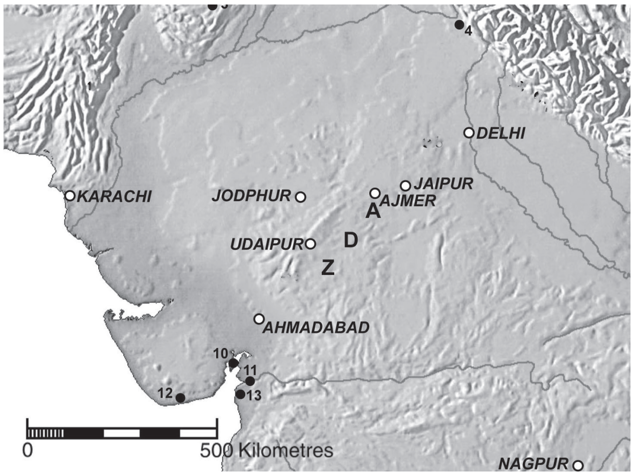

Fig. 1. Location of Zawar, Dariba and Agucha (Z, D and A) together with some sites in north western India and surroundings mentioned in the text 4 Kwanu; 10 Khambhat (ancient Cambay); 11 Bharuch (ancient Barugaza or Broach); 12 Diu; 13 Surat. (A Simpson).

monographs,[1] and thus it seemed appropriate to bring together the wide ranging new information to attempt a new overview of the history of zinc, now common place, but whose extractive metallurgy played a major role in the development of chemical industry.

2. Copper-Zinc Alloys before Metallic Zinc

2.1 Very early instances of Copper alloy Artefacts containing Zinc

Rather unexpectedly alloys of copper and zinc are known almost from the inception of metallurgy. The situation is somewhat confused because certain well publicised examples have been shown not have been of brass at all.[2] Others, such as those listed by Caley (1964, pp.6-12) are likely to be of brass but lack any archaeological provenance, and are not now considered ancient (Craddock, 1978; Bayley, 1998). However, there remains a residuum of very early copper alloy artefacts from controlled archaeological excavations around the world that have been shown to contain substantial quantities of zinc (Thornton, 2007). The more significant finds include material from pre-Hispanic Argentina (González, 1979), South West Asia (Thornton, 2007) and China (Zhou, 2001). The copper alloys from Argentina contained up to 7%. Thornton et al. (2002) in the course of analysing a large number of copper alloy artefacts from Tepe Yahya in Iran dating to the early second millennium BCE, identified three copper alloy ornament fragments containing zinc, and noting that they were not unique, proceeded to collect other published examples of early copper alloy artefacts with significant zinc contents from Greece to North West India (Thornton, 2007). Excavations in China have produced a number of tiny copper alloy fragments or artefacts apparently containing over 30% of zinc, dated to the fourth and third millennia BCE (Sun and Han, 1981), the first was not beyond suspicions over their archaeological context. However, similar pieces containing zinc have also been excavated from other sites, and recent analyses shows that the zinc contents actually lie between 20 and 32% (Zhou, 2001).

These early examples of copper alloys containing zinc raise questions of how they came about and if their production was deliberate. As Thornton (2007) stated, in the absence of zinc metal, either zinc minerals could be added to molten, or at least very hot, copper , alternatively

[1] These include Kharakwal (2011) on zinc and brass in India generally, and more specifically Kumar (2017) deals with the history of Zawar and Craddock (2017) deals with the archaeology of Zawar and related sites in Rajasthan. At the same time there have been detailed historical studies on the traditional Chinese zinc industry (Craddock and Zhou, 2003) and a major programme of excavation of early zinc smelting sites (Liu, et al., 2007) and the scientific study of the remains to establish the parameters of the process (Zhou, et al., 2012; Zhou, 2016).

[2] In the analytical tables in the original report on the excavations at Lothal (Lal, 1985) one piece (4189) was reported as containing about 6% of zinc and was thus regarded as the first Indian brass. However subsequent enquiries have shown this to be the result of a typographic error (Kenoyer and Miller, 1999, Appendix A).

a mixture of copper and zinc minerals, most likely a naturally-occurring zinc-rich copper ore, could be smelted. A number of experiments have been conducted smelting oxidised copper ores and zinc oxide in crucibles, discussed below, produced copper with up to 40% of zinc, strongly suggesting that the adventitious smelting of an oxidised zinc-rich copper ore could produce a natural copper-zinc alloy.[3] This would be encouraged if the smelting environment was very reducing which would encourage the reduction of the zinc minerals, and the temperatures were comparatively low, encouraging its retention in the copper. It is believed that the earliest copper smelting probably did take place in crucibles, but although the temperatures were relatively low, the conditions were generally relatively oxidising compared to the smelting conditions in later furnaces (Craddock, 1995, p.135). Thus the relative scarcity of zinc-rich copper ores and the very reducing conditions necessary, combine to explain the paucity of ancient copper alloys containing more than traces of zinc.

This leads to the second question of whether the known examples are likely to have been deliberate productions. This is difficult to resolve with any certainty, but it is noticeable that most of the examples also contain arsenic or tin, suggesting that the smiths were not aware of the presence of another metal. Furthermore, these early examples have no preferred zinc content. It is also noticeable that there are no specific types of artefact that are made of the zinc-rich alloys; rather they occur randomly alongside similar artefacts containing no zinc (see Thornton, 2007, Fig. 3, for example). This evidence suggests that in examples before about the mid second millennium BCE the presence of zinc was fortuitous. This was set to change through the next thousand years or so.

2.2 'Copper of the Mountain,' *Oreichalkos*, and the first deliberate Brasses

Several examples of copper alloys between about 6 and 15 per cent of zinc have been identified coming from the Near and Middle East from the later second millennium BCE (Craddock, 1978, updated by Bayley, 1998), between 12 and 15% of zinc from Nuzi, Iraq (Bedore and Dixon, 1998) and a finger ring with about 12% of zinc from Ugarit, Syria (Schaeffer-Forrer, et al., 1982). Several of the 'bronze' bowls excavated from Assyrian Nimrud of the 7th century BCE also contain significant quantities of zinc (Hughes, et al., 1988). At just this time the Assyrian records make reference to a special copper, 'copper of the mountain' (Halleux, 1973). References to 'special' coppers occur throughout the literature of antiquity, but this one is of especial interest to the study of brass as very soon afterwards there are references in Greek literature to *oreichalkos*, literally 'copper of the mountain', in what has become known as the Orientalising phase of Greek culture in the seventh and sixth centuries BC, when many ideas were absorbed from Greece's neighbours to the East. References to *oreichalkos* continue through the first millennium BC, and together with its Latin derivative, *aurichalcum*, there is no doubt that by the end of the millennium the words referred to brass. It seems likely that the original 'copper of the mountain' was obtained by smelting a natural copper-zinc ore, but at some time this would have changed to a more assured production by the addition of zinc minerals to copper. It is possible that a memory of this transition is preserved in Pliny's statement in the *Natural History* (N.H. 34. 2-4, Rackham, 1952, p.129) that the ore producing *aurichalcum* was long since exhausted, but that the copper now obtained from other locations readily absorbed *cadmea*.

[3] Although no one seems to have tried to smelt a naturally occurring copper-zinc ore, probably because they are usually sulphidic.

3. Brass in the Hellenistic and Roman World

Although production of brass is likely to have become increasingly common through the last centuries of the first millennium BCE across a broad band stretching from Greece to India, the earliest series of artefacts made exclusively from brass, so far identified, date to no earlier than the beginning of the first century CE. These are the coins issued by Mithrades VI in Phrygia and Bithynia (Fig. 2) and contain issues of unalloyed copper as well as others of bronze and brass containing about 20% of zinc (Craddock, et al., 1980).These are of some importance as they are ancestral to the reformed coinage of Eastern Empire undertaken by Augustus in 27 BCE, with issues of the copper *ass* and the brass Augustus C coins (Burnett, et al., 1982). These issues were shortly followed by the general reform of the coinage throughout the Empire in 23 BCE, with the copper *as* and the brass *dupondii* and *sestertii* (Caley, 1964; Grant, 1946; Riederer, 1974; Furger and Riederer, 1995).

Fig. 2. The earliest brasses: Coins. Top row: Pergamum, mid first millennium BC. Middle row: SC coins of the eastern Roman reformed coinage of 27 BCE. Bottom row: Roman *Dupondius* and *Sesstertius* of the general reform of 23 BCE.

The adoption of the alloy by the Romans at least, was probably rather more rapid than suggested by these major coin issues. Relatively few copper-base coins were issued by the central mints through the first century BCE, but one issue of coins by Julius Caesar in 55 BCE are of brass (Grant, 1946). At just this time the well-known *alesia*-type brooches began to be produced and they were always made of brass containing about 20% of zinc (Istenic and Šmit, 2007). These brooches are associated with the military and thereafter at least for the next century most Roman military copper alloy metalwork was made of brass (Craddock and Lambert, 1985; Jackson and Craddock, 1995). The combined effect of the regular use of enormous quantities of brass for coins and military fittings was to spread the metal throughout the Empire and beyond. Bronze certainly continued in production and thus inevitably there was an ever-growing volume of copper alloy artefacts containing both zinc and tin, resulting at least initially in the chance mixing of scrap brasses and bronzes (Craddock, 1978; Dungworth, 1997; Bayley and Butcher, 2004). However, such ternary alloys do have superior properties to the binary alloys and since the Post Medieval period at least, they have been deliberately produced and are known in English as gun metals, but their qualities may have been recognised earlier (Furger and Riederer, 1995). Similarly, Dungworth (1996) believed there was a deliberate changeover from brass to leaded brass for coins in the late Roman Empire.

Earle Caley (1964) suggested on the basis of a very few coin analyses and the remarks of Pliny, that brass making had in effect already become a lost art by the middle of the first century CE. Although this was certainly not the case, it is true that the zinc content of brass coins and their incidence did decline through much of the Roman Empire. Dungworth (1996) showed that although other alloys, notably leaded bronze, became popular, the incidence of zinc in the copper-base could not be explained simply by the use of scrap, but required an input of fresh brass. Similarly, the analytical studies of Craddock (1978) and Dungworth (1997), together amounting to several thousand analyses of a wide range of everyday items through the first four centuries of the Roman Empire, also showed that fresh brass was being used alongside bronze and leaded bronze. On this basis it was assumed that the replacement of bronze by brass as the usual copper alloy proceeded uniformly, that is the zinc content steadily increased in a wide range of artefacts across the western parts of Eurasia (Craddock, 1978). More focused typological and regional analytical programmes such as those of Carradice and Cowell (1987) on coins and Bayley (1998) and Bayley and Butcher (2004) on brooches have shown that specific regional issues of coins or types of brooch could be of brass whilst their immediate contemporaries were of bronze.

Whilst the Roman Empire held together supplies of both tin and zinc were assured with tin coming from the mines in Iberia and Britannia, within the Empire, and with easy access to the sources in Central Europe (Penhallurick, 1986). Zinc was available from the major smithsonite zinc deposits in the north west of Gaul (and possibly also from Britannia) and from the sphalerite deposits in Anatolia. With the breakup of the Empire the sources in the west were lost.[4] Thus it comes as no surprise to learn that in the Byzantine Empire which succeeded the Romans in the East, the copper alloys were predominantly of brass. Conversely the very earliest Islamic metalwork reverted to bronze until the zinc sources in Anatolia and in Iran came under their control (Schweizer and Bujard, 1994; Ponting, 2003). Thereafter, the Islamic world from Spain to Delhi used brass almost exclusively except for special items such as mortars and mirrors (Craddock, et al., 1998a).

In post-Roman Europe similar regional and cultural factors are apparent. Thus whilst a broad band across central and western Europe from Scandinavia down to Italy and Spain favoured brass (but not exclusively), the Celtic west and Eastern Europe utilised bronze almost exclusively right through until the end of the first millennium CE (Craddock, 2001).

4. Brass Production in Classical Antiquity

Pliny's statement in the *Natural History* (N.H. 34. 2-4; Rackham,1952, pp.126-8) that the ore producing *aurichalcum* was long since exhausted, but that the copper now obtained from other locations readily absorbed *cadmea*, is one of the few that statements, albeit with extreme brevity, of how brass was actually produced in Classical antiquity.

Cadmea is very likely to have been zinc oxide, of which there were two potential minerals, either smithsonite (the old calamine), $ZnCO_3$, or the more common sphalerite (the old zinc blende), ZnS. It would only have been a matter of time before it was discovered that by adding the zinc oxide so formed to molten copper that an artificial *oreichalkos* could be made.

Deposits of smithsonite are generally less prevalent in the broad band stretching from the Mediterranean to India, but major deposits occurred both in China and in Western Europe. Smithsonite could be used directly after calcination, but the more prevalent sphalerite ores had to be carefully roasted and sublimated to remove the sulphur and create the oxide.

4.1 Production of Zinc Oxide

Sphalerite minerals are commonly found in association with lead ores and there is some suggestion that zinc oxide was produced, initially at least, as a by-product of the production of silver from argentiferous lead. Pliny stated (NH 34.100,

[4] Although there are records of intrepid merchants in the 6th and 7th centuries CE voyaging from Coptic Egypt all the way to Britain in search of tin (Penhallurick, 1986, p.237)

Rackham, 1952, pp.201-2) stated that: 'This *cadmea* is certainly also produced in furnaces where silver is smelted', before going on to give a long account of the different varieties to be collected from various parts of the furnaces and flues. There was also a similar very material known as *lauriotos*, presumably deriving its name from the Athenian silver mines at Laurion (N.H. 34.132, Rackham, 1952, pp.223-5).

The most detailed early descriptions of the production of zinc oxide from its ores are those given by Dioscorides Compiled in the first century CE in his *Materia Medica* (Book V, Chapter 84, Gunther, 1934: pp.623-5). The translations which follow were originally made by John Goodyer in 1655, hence the archaic English, and republished by Gunther:

> But Pompholyx [calcined smithsonite, zinc oxide] is also made from Cadmia purposely blown with ye bellows for ye making of it. And it is made thus. In an house having a double roof a chimney is built, and by it towards ye loft, a suitable window, and open at ye parts above. But ye wall of ye house next to ye chimney, is beaten through with a small hole, into the very furnace for ye receiving of the bellows. It hath also a proportionable door made for ye going in, and coming out of the workman. There is joined unto this room another room, wherein ye bellows and ye bellows-blower work. Then the coals are put into ye furnace and kindled, afterward ye workman standing by doth sprinkle on from ye places over the head of the furnace the Cadmia being beaten small. And ye servant that is under withall doth do ye same, and casteth on more coals, until all ye Cadmia that was laid on be consumed, so that by the burning, the thin and light part is carried into the upper room, and sticks to the walls and to the roof thereof. But the body that is made of the those things carried up, at ye beginning indeed is like to ye bubbles standing upon ye waters, but at last more increase coming, it is like to the fleeces of wool. But that which is heavier goeth into ye places under foot and is dispersed about, some to ye furnace, and some to ye floor of ye house. This is thought to be worse than that of thin parts, because it is earthy and full of filth by ye gathering of it.

A broadly similar arrangement for collecting the zinc oxide fume from above the silver smelting furnaces in Post Medieval Europe was described and illustrated in Agricola's *De re Metallica* (Hoover and Hoover 1912, p.395) (Fig. 3). Note that there is a clear distinction between the purity of the sublimed material collected from above the furnace which should equate with the flat plates of sublimate from contemporary Zawar illustrated in Figs 5 & 6, and the material remaining in and around the furnace.

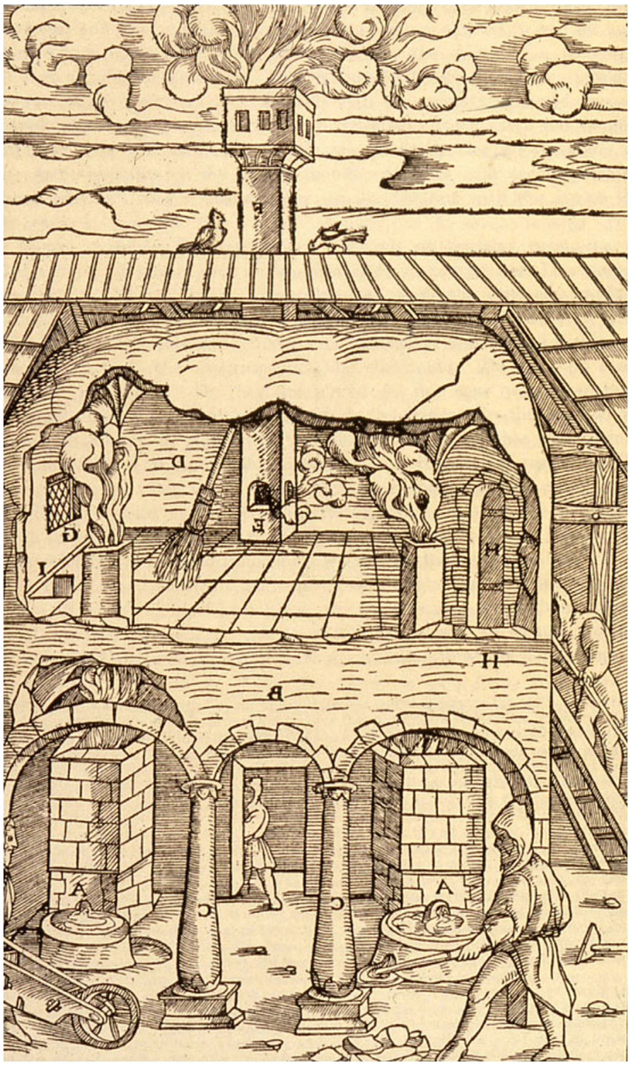

Fig. 3. Furnace arrangement for collecting ZnO sublimate in 16th century central Europe. Very similar to the descriptions given by Dioscorides 1500 years previously (from Agricola, Hoover and Hoover, 1912, p.395)

Dioscorides also described a very different arrangement for the production of calcined zinc oxide, this time actually from brass.

> But Cadmia also comes from brass red hot in a furnace, the soot sticking to the sides, and to ye top of the furnaces. Now [rods] of iron, of a great bigness, called by ye metal men acestides are joined together at ye top to ye end that ye bodies that are carried up from the brass may be held and settled there, which also sticking ye more, grow into a body, and sometimes one kind of it, sometimes two, or all are made.

He continues that it is also produced from ore in this manner in Cyprus, one of the main sources of copper in Classical antiquity.

It is made also of a burned stone called Purites digged out of an hill that lies over Solis [Cyprus]

4.2 Production of Brass

Brass could have been made either by adding the zinc oxide so produced directly to molten copper in closed crucibles containing charcoal or by the more familiar cementation process of the last few centuries[5]. In this the zinc oxide was added to thin foils or finely divided zinc in the solid state in a closed crucible with charcoal, at temperatures hot enough to produce a zinc vapour (>907^0 C) but well below the melting point of copper (1083^0 C).

As noted above the descriptions of brass making in antiquity are generally lacking in detail, Pliny stated that 'The highest reputation has now gone to the Marius copper, also called Cordova copper; …. this kind most readily absorbs *cadmea* and reproduces the excellence of *aurichalcum* (N.H. 34.4, Rackham, 1952, p.128). However two Medieval Western sources do offer some detail, these are the 12th century descriptions of Theophilus in Europe (Hawthorne and Smith, 1963) and the 10th century descriptions of al Hamdani in the Middle East, (Toll, 1968). These sources both unequivocally state that the zinc minerals, from whatever source, were to be added to molten copper.

Thus this was not a solid state process cementation process (Craddock and Eckstein, 2003). Others (Rehren, 1999a & b) have claimed that the cementation process was already carried out in Classical antiquity. At the temperature of molten copper (~1100^0 C) the process would have been relatively quick but the vapour pressure of the zinc in the copper would have reduced the amount absorbed. By operating at the lower cementation temperature, ideally between about 900^0 C and 1,000^0 C for much longer periods more zinc could be retained.[6]

There are some references to *cadmea* in the various versions of the *Mappae Clavicula*, of which the most complete was compiled in the 12th century from earlier sources (Smith and Hawthorne, 1974, pp.31-2). In Recipe 9, *cadmea* is to be added to a molten alloy of gold and copper until it appears as perfect gold and in Recipe 18, *cadmea* is to be added to either an unknown material called *armenium* or to copper to make gold. However, Recipe 74, (p.38), describes the

[5] There is also a possibility that brass may have already been made in on a very minor scale by mixing the two metals (*speltering*). This is the description made in the 4th century BC by Theopompous, later recorded by Strabo, of the occurrence of droplets of metallic zinc during the smelting of argentiferous lead-zinc ores, which could then be used to make *oreichalkos* (see below). In Craddock (1998) it was suggested that the first artificial *oreichalkos*, or brass, was produced on a regular basis in this manner using metallic zinc, as a by-product of silver smelting. However, study of the remains from Zawar (see below) and Post Medieval descriptions of the same phenomena (see below) suggest that the zinc so produced must inevitably been imbedded in zinc oxide and thus it is more likely that the first brasses could have been made by adding the zinc oxide to molten copper, and that the precocious production of brass by mixing two metals related in Theopompous' account was never more than the scientific curiosity it had certainly become by the time Strabo came to repeat it in the first century BCE.

[6] Haedecke (1973) suggested 970^{0}C as the optimum.

making of brass from sheets of refined copper, which is a cementation process:

> These are to spread out on the bottom [of a pot] and sprinkled with white *cadmea*. Then, lute the furnace thoroughly with potter's clay so that it cannot breathe for a day. Then open it up and if it is good, use it; if not, cook it with *cadmea* a second time, as above. If it comes out well, the *caldarium* copper is permeated throughout with gold (colour).

Significantly, Smith and Hawthorne point out that an earlier version of this same recipe states that the copper is to be molten during the conversion, and suggest that this is the more likely version. However, could it not be that although the earlier version perpetuated the old classical method, some inkling of the more advanced cementation processes practiced in India and China had already become known in the Mediterranean world by the 12th century.

Possibly the composition of Roman brasses might give some indication as to which process was used. It has been claimed that the maximum amount of zinc that could be absorbed by the copper in the direct process was 28% (Craddock, 1978). This figure was based on the experiments carried out by Werner and by Haedecke (Werner, 1970: Haedecke, 1973), analytical data on early brasses likely to have been made by the direct process and the claims of some early technical writers such as Ercker (29%) (Sisco and Smith, 1951, p. 257) and actual brassmakers such as Nehemiah Champion (28%) (Day, 1973, pp. 61-2).[7] Some of the 16th century descriptions state that the copper should be in finely divided state (Agricola's *De Natura Fossilium* of 1546, Bandy and Bandy, 2004, p187 and Biringuccio's *Pirotechnia*, Smith and Gnudi, 1942, p.72), but none of them lay any emphasis on keeping the temperature of the process below the melting point of the forming brass until the conclusion of the process, in fact Biringuccio specifically states that the crucibles should be held at the melting temperature. The first European description of what seems to be a true cementation process, emphasising that the copper must be remain finely divided and solid until the end of the process, only occur from the 17th century, more or less coincident with the rise in the maximum zinc content found in brasses from 28 to 33% (see below). Several of the 18th and 19th descriptions concur that the maximum zinc content that could be achieved was in the region of 33.3% (Swedenborg in 1734 [34%], Searle trans., 1938, p.334; Champion in 1730 [33%], Day, 1973, pp.61-2; Franz Matthias Ellmayrs in the 1780s [29.5%], Priesner, 1997, p.175). In the final days of the cementation process in the mid19th century 33.3% (i.e. 1 part zinc to 2 parts copper) was still quoted as the maximum zinc content (Percy, 1861, p.616).

Through this period the zinc content of European brasses rose steadily (Werner, 1970) and after about 1500 CE an increasing number have in excess of 30% of zinc (Cameron, 1974; Caple, 1995; Craddock, 2000/1; Pollard and Heron, 1996). This could be due to improvements in brass making technology by the direct method or the beginning of the production of brass by the mixing of copper and zinc metals (*speltering*), or the first import of zinc from Asia in the vessels of the European trading companies. The determination of which method was used for any particular brass is complex and not easily resolved.

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[7] These figures were contested by Welter (2003), based on his own experiments and those of Ullwer (2001& 2008), which showed that copper could be induced to accept up to 40% of zinc oxide, and experiments by Zwicker, et al. (1985) and Sun and Han (1981) also succeeded in making small quantities of brass by the direct method containing well in excess of 40% of zinc. However it still remains true that few if any of the genuine artefacts analysed have in excess of 28% of zinc prior to the 16th century and all Post Medieval and later sources stated quite clearly that 33% was the very maximum attainable.

5. Brass in Ancient India

5.1 The first Brasses

As yet little metalwork from the archaeological excavations carried out at the large urban sites of the first millennium BCE has been analysed. Kharakwal (2011, pp.83-115) has brought together examples of early brasses from India, and from these there is growing evidence for copper alloys containing zinc. Brass seems more prevalent in the far north west of the region. Analysis of 39 copper alloy artefacts from the excavations carried out at Taxila, now in northern Pakistan, near to Rawalpindi (Ullah and Marshall 1951, pp. 567-9; Prakash and Rawat 1965, pp.50-1, table 5.3) dating from the latter part of the first millennium BCE and into the first centuries CE revealed a wide range of alloys, including high tin bronze, one cupro nickel item, and four of brass. The brasses had zinc contents of 13.07%, 12.88%, 19.7% & 34.4% with small amounts of tin and lead. The brass with 34.4% of zinc was from the neck of a metal vessel dated to around 300 BCE, and also contained 4.25% of tin, 3.08% of lead together with 0.26% of antimony, 0.4% of nickel and 1.77% of iron. Some small copper alloy rods and bangles from the site of Senuwar in the Kaimur region of the Ganges Valley dated to the early centuries CE are mainly of copper with a few percent of zinc, but two have 35-36% of zinc with only traces of other metals (Singh, 2004). These are very high zinc contents for brass made by the direct process and thus could be taken as evidence for speltering, or at least the cementation process (see above). However, it is necessary to be cautious, the upper limit of zinc absorption of 33.3% by cementation is very close to the figures given here, and so far only three such pieces have been located, thus it perhaps unwise to take these analyses as certain evidence for the production of metallic zinc. It is just possible that small quantities of metallic zinc could have been recovered during the smelting of silver ores and used to make brass (see 'production as a by-product below).

5.2 The Production of Brass in Ancient India

> It appears probable to me, that brass was made in the most remote ages in India, and in other parts of Asia, of copper and calamine, as it is at present. (Watson, 1796, p.106)

The evidence of early brass production in India is much stronger than in the West, with detailed literary sources, now reinforced by the material evidence from the excavations conducted at Zawar (Craddock, et al., 1998b; 1998c; Craddock and Eckstein, 2003; Craddock, 2017).

5.2.1 The Ores

The *Rasārṇavam Rasatantram*, normally referred to just as the *Rasārṇava*, lists three kinds of zinc ore, before going on to describe how they may be used to make brass. The date of the work is very uncertain, Tripathi (1978, p.6) would date it to the second part of the first millennium BCE, but this would seem too early, especially as many of the processes involve mercury and would seem to be Tantric in origin, and thus not dating before the mid-first millennium CE . Ray (1956, p.118) dated it to the 12th century CE, which is more likely. The description of brass production is also included in the compilation made by Todarananda in the 16th century (Dash and Kashyap, 1994, pp.328-31)

The three types of zinc ores (*rasaka*) are described in the *Rasārṇava* at VII 31-4 (Ray, 1956, p.138) are as follows:

I. *Marica rasaka*, which was described as the best quality and like yellow-coloured soil. This is almost certainly smithsonite (calamine), zinc carbonate, $ZnCO_3$.

II. *Guḍa (jaggary) rasaka,* which was described as being of medium quality and was the colour of treacle. This is probably sphalerite (blende), zinc sulphide, ZnS.

III. *Puṣan rasaka*, which was described as being the poorest quality, and was hard like stone. This could be either hemimorphite, the hydroxy silicate, $Zn_4Si_2O_7.(OH)_2.H_2O$ or willemite, $ZnSiO_4$, both of which form in the upper, oxidised parts of the ore body, although apparently not at Zawar.

This is one of the few descriptions of the main zinc ores; elsewhere the general term *rasaka* for zinc ore is used without further elaboration, and which most modern translators assume to be calamine (smithsonite), zinc carbonate, whereas in fact smithsonite is rare in the Indian deposits, the usual ore is sphalerite, the sulphide.

5.2.2 The Production of zinc oxide: The Evidence from Zawar

The major Mauryan mining sites in the Aravalli Hills were engaged in the production of silver (Craddock, et al., 2013; Craddock, 2017) with probable exception of Zawar. This was similarly a very major Mauryan mining enterprise but almost certainly for the production of zinc oxide (Craddock, 2017). The smelting evidence from contemporary Zawar is very different from the other mines although the ores are fundamentally the same, comprising sphalerite, galena and pyrites (Craddock, 2017). In particular the early slags at Zawar all derive from smelting an ore in the oxidised state. In amongst the slags are fragments of furnace lining including rim fragments with crusts rich in silica and the oxides of zinc and lead. These crusts also contain some lead and zinc sulphides. The presence of the sulphides does confirm that the ores used were originally sulphidic. It would seem most likely that the crusts had formed on the upper surfaces of a furnace where initially sulphidic ores were being charged to the furnace and roasted to convert them to oxides. This was followed by a more reducing process during which the zinc and lead vapours formed, reoxidised and some were deposited on top of the unchanged sulphide ore dust on the upper sides of the furnace.

A second group of material comprises thin flat plates of high density made up of layers of zinc and lead oxides (Figs. 5 & 6). The layers are quite distinct, the lead-rich layers are yellow-white in colour whereas the zinc rich-layers are green, recalling the ancient Sanskrit and Greek descriptions of layered zinc oxide (see above), suggesting a progressive build-up. Such plates have not been recognised at any other smelting sites within India but have been reported from contemporary Cyprus (Zwicker, 1992), where the production of zinc oxide was also performed (see above).

The most tenable interpretation for the finds from the early slag heaps is that they represent the debris from a multi-stage process to produce zinc oxide, which may be reconstructed as follows (Fig. 4). The beneficiated sulphidic ore which would have been predominantly of zinc sulphide but with some lead and iron sulphide present, would have been roasted in the pre-heated small shaft furnaces to convert the bulk of the zinc sulphide to the oxide, while at the same time oxidising the lead and iron sulphides. When it was judged that the oxidation was complete the conditions would have been made much more reducing and the zinc oxide was reduced to produce clouds of zinc vapour that would have promptly oxidised in the flue and then been deposited as a sublimate against flat ceramic

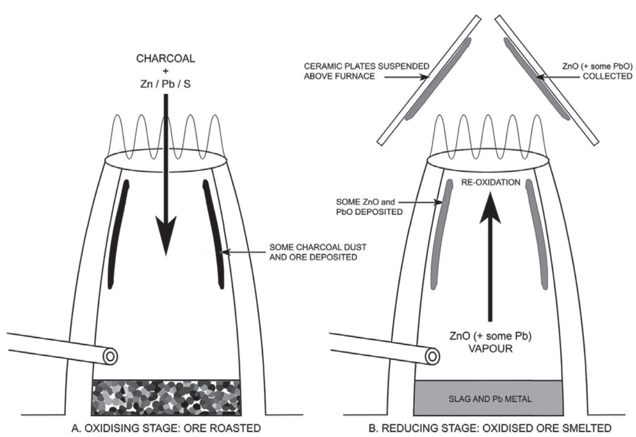

Fig. 4. Conjectural smelting arrangement for the two-stage production and collection of ZnO at Zawar. (cf Fig. 3).

baffles that were positioned above the furnace. Almost all of the sulphur was removed in this operation, which was necessary before the mineral could be used in the production of brass.

The dates for this operation at Zawar are mainly from the Mauryan era, in the second half of the first millennium BCE, but some production continued as late as the 7th century CE, shortly before the production of zinc metal commenced there.

5.3 The Production of Brass

There is a brief reference to the production of brass by a direct process in the *Rasaratnākara*, but it is not certain whether the cementation process is meant or the addition of the mineral to molten copper. This work is believed to have been compiled by the greatest of the early Indian scientists, Nāgārjuna, who probably lived at some time in the second to fourth centuries CE. In its present form it probably belongs to the seventh or eighth centuries CE and also includes a description of the preparation of metallic zinc (see below). It states that:

> What a wonder is it that zinc ore ….roasted three times with copper converts the latter to gold? **3** (Ray, 1956, p.129)

Brass making is also described in the *Rasārṇava,* the description is clearly directly derived from the *Rasaratnākara*, and is as follows:

> What a wonder is it that *rasaka* mixed with certain organic matter and roasted three times with copper becomes gold ? VII 37-8 (Ray, 1956, p.138)

5.3.1 Brass production by the Cementation Process

In the *Rasārṇavakalpa* which is believed to have been compiled between the 10th and 12th centuries CE, a more explicit description of the production of brass is given:

> One *māsa* of the powder of blue vitriol (*tuttha*)[8] and an equal weight of copper leaves are to be placed in order on the above substances (killed sulphur and the four alkaline substances).

Another recipe

> One *māsa* of *rasaka* (translated as calamine, but roasted sphalerite seems more likely) is to be arranged on it (i.e. the copper leaves). Powdered *kāca* (salt) again arranged all over the substances. The mouth of the crucible is to be sealed. (370-1)
>
> The whole substance thus contained in the crucible is to be roasted over a fire of cow dung, until the copper becomes liquid. This copper will, no doubt, assume the form of gold, displaying eight shines. (372) (Roy and Subbarayappa, 1976).

[8] A real problem occurs with the identification of the word *tuttha* in the Indian context. In the *Arthaśāstra*, compiled in the late first millennium BC. Kangle (1972), Shamasastri (1915) and Meyer (1925/6) translate *asthituttha* as blue vitriol, that is copper sulphate. The justification for this is that there is a much later medieval reference to *tuttha* being formed by the action of 'burning water' on copper. Presumably the burning water is acid, more likely to have been nitric acid made from potassium and sodium nitrate, saltpetre, the Indus earth of the alchemists, than the sulphuric acid necessary to make copper sulphate, blue vitriol, but the reference would suggest that a copper salt formed. Some medieval Islamic sources also state that *tūtīyā* was the vapour from copper, but in contexts where it must be zinc oxide. It is possible here that the Islamic sources were referring to the heating of brass to cause the zinc to evaporate as zinc oxide, as described in Dioscorides (see above). *Tūtīyā* was the usual term for zinc oxide generally in Islamic treatises (Allan 1979, pp.39-45; Craddock, et al*.,* 1998a). For example *tūtīyā* was the material mined at Zawar according to the *Āīn-i Akbarī*.

Kangle discusses these and the opinions of the other commentators on the *Arthaśāstra* in some detail and suggested that *tuttha* could be translated as the basic material or earth from which the crucible or cupel was made; earth and bones, earth and lead etc, or that *tuttha* refers to materials added to the silver with the lead in cupellation process. He pointed out in one reference *tuttha* seems to be the name of a locality, but elsewhere translated *tuttha* just as being the crucible or cupel. Falk (1991) suggested that *tuttha* should be translated as zinc ores, being related to the Sanskrit and Old Persian word *tūtīyā* which literally means smoke, plausibly derived from the clouds of zinc oxide sublimate produced when zinc ores are smelted in conventional furnaces, Zawar according to the *Āīn-i Akbarī*.

Fig. 5. Flat plates of layered ZnO and PbO. Zawar, early centuries AD.

Fig. 6. Flat plates of layered ZnO and PbO, showing layering. Zawar, early centuries AD.

Although these are very short descriptions of brass making, they are nonetheless of great interest. The zinc minerals are roasted with copper leaves in the presence of other materials and are clearly genuine cementation processes where the copper remains in a solid state throughout whilst being converted to brass by exposure to zinc vapour.

These would seem to be the latest references in the Indian literature to the production of brass by treating copper with zinc ore. As metallic zinc was already being prepared as an industrial commodity, with descriptions of laboratory preparation given in both the *Rasaratnākara* and the *Rasārṇava* (see below), henceforth brass was presumably made by mixing copper and zinc metals (*speltering*).

6. Brass in China

Brass was very uncommon in the Far East before the mid second millennium CE. However, there were some brasses dating from the beginning of the first millennium CE, known as *tutty*, *tou* or *toushi*, the words apparently derived from the Indian *tutiyah*. References to the metal make it clear that it was coming from the West along the Silk Road and was associated with the Buddhist monks coming from South Asia (Zhou, 2001). *Toushi* remained highly prized and very expensive through the first millennium CE, and the earliest description of its manufacture dates from the beginning of the Song dynasty at the end of the first millennium CE. The process was described in some detail. It states that one *catty* of pure copper mixed with one *catty* of zinc ore are to be mixed and heated in a closed iron box for two days and nights. After further firing in a reducing stove for six hours the product were beautiful pellets. The length of time, the specification of an iron box in which it would have been unsuitable to melt the copper and the statement that the product was also a solid, all strongly suggest that this was a true cementation process. Thereafter brass production progressed, and from this the production of metallic zinc is believed to have evolved (Zhou, 2007, and see below).

7. Zinc Metal

7.1 Early Examples

So far only one piece of metallic zinc that had been worked has been recognised from antiquity. This is the small thin sheet excavated from Hellenistic deposits in the Athenian Agora (Farnsworth, et al., 1949). The term 'recognised' is used somewhat advisedly as on excavation the piece was believed to be lead, and was being cleaned in acid when the violent efflorescence led to the realisation, that it must be something else, just in time to save it from total dissolution. Subsequent examination showed that it was of zinc with 1.3% of lead and other traces and had been cold-hammered to shape.

7.2 Production as a by-product

Zinc is not infrequently associated with of the ores of other metals, most notably argentiferous lead. During the smelting of these ores some zinc is reduced and appears as a zinc vapour which promptly oxidised to form clouds of white zinc oxide some of which settled on the upper parts of the flues as described in more detail above. Occasionally just a very little of the zinc condensed to metal before oxidisation and was present as droplets in the zinc oxide. The phenomenon was recorded as occurring at the silver mines near Andeira (modern Balya Maden) in Phrygia by the Greek geographer, Theopompus of Chios, in his *Philipicca* compiled in the fourth century BCE, and although the original account is lost parts are preserved in Strabo's *Geography* (13.56, Jones, 1928, vol. 6, p.115; and see Craddock, 1998 for a full discussion). The ores at these mines were argentiferous mixed lead-zinc-iron sulphides, which on smelting, in addition to the argentiferous lead, produced drops of 'false silver'. This, when added to copper gave *oreichalkos*. Andeira was not the only ancient smelter to produce zinc as modern excavations are beginning to reveal. For example two small pieces of zinc, containing about five percent of lead, were found in a metal workshop at Kakusowice, 50 km north east of Krakow in Poland contemporary to the Late Roman period (Stos-Gale, 1993, esp. p.115). Another piece of zinc was excavated from first century CE contexts at the Roman lead mine at Charterhouse on Mendip in Somerset, UK (Todd, 2007). The lead ores at the latter site contain zinc and the small lump was almost certainly adventitiously produced in flues of the lead furnaces, and as the piece was unworked, it is quite possible that it had not even been noticed.

Thereafter there is no mention of such adventitious zinc until the later Middle Ages in Europe, when *conterfei* was recorded as occurring during the smelting of argentiferous lead-zinc ores at Rammelsberg by Agricola in his *De re Metallica* of 1556, and which his later editors, the Hoover's, identified as being zinc (Hoover and Hoover, 1912, p.408). Ercker in his *Treatise* of 1574 (Sisco and Smith, 1951, p.271) stated that:

> Finally, I should not leave unmentioned that in the furnaces in which the lead ore of Goslar (Rammelsberg) is smelted, a gray matter mixed with yellow is deposited during each campaign on all four walls of the furnace, in the thickness of a straw. This is called calamine and is used as an addition in making brass, as you were told at the end of the Third book. After every eighth or ninth campaign the smelters must knock this matter out of the furnaces, which otherwise would become too narrow, and eventually efficient and profitable smelting would no longer be possible therein (Fig. 7).

The *conterfei* and 'grey matter' could well have been droplets of metallic zinc, or possibly

Fig. 7. Scraping ZnO off the furnace walls at the silver smelters at Rammelsberg, Germany, in the 16th century. (From Ecrker, Sisco and Smith, 1951)

zinc oxide. There is no hint in either of these two accounts that the zinc metal, if such it was, was in any way valued or separately collected. A more detailed record was given by Georg Engelhard Löhneiss in his 1617 *Bericht von Bergwerken* (Sisco and Smith, 1949; see also Partington, 1961, p.108) where it stated that:

> When the smelters smelt (the Rammelsberg lead ore) there collects in the joints down in the front wall of the furnace, where the spaces between the slates have not been plastered tightly, a metal which they call zinc or *counterfeit*. When they knock against the front wall this metal runs out into a pan that has been placed beneath. This metal is white like tin, but harder and less ductile, and rings like a little bell. A large amount of this *conterfeit* could be produced if an effort were made, but since it is little valued the helpers and the smelters do not exert themselves (though it might be worth it), and they produce only that which collects incidentally in the front wall. They do not even knock it out after every campaign but only when someone has asked them for it and they can expect to be tipped. There are some campaigns during which much larger amounts collect that during others. On some occasions they knock out about two pounds (approx. 1 kg) at a time, and at others not even three or four *lot* (approx. 100 gm).

It should be noted that this account detailed and accurate though it is makes no reference to the use of the metal to make a superior brass, which was always the main function of the zinc imported into Europe from the east. As these imports became established through the 16th and 17th centuries so it is likely that the Rammelsberg counterfrei or zinckum, was recognised as being identical to the imported metal and more systematically collected. Thus in 1700, Stahl (Partington, 1961, ps.108 & 682) described the deliberate collection of the metallic zinc at Rammelsberg by cooling the flues with water. The metal so condensed was shaken down from the flues, melted on a gentle fire and cast into pigs. Later still in 1734 Emmanuel Swedenborg in his *Regnum Subterraneum sive Minerale de Cupro et Orichalo* (Sisco and Smith, 1951, p.272) stated that an internal slab was built into the furnace to protect the condensing zinc from the oxidising blast, and that no less than seven or eight tons of metal were produce annually, although no more than two kg per smelt. Shortly after this report, zinc smelting in its own right commenced in Europe at Bristol and the importance of this source of zinc as a by-product diminished, although Goslar (Rammelsberg) zinc was still available to Watson (1796, p.40) at the end of the century. Percy (1861, p.519) recorded that drops of zinc trickled down from the tuyere at the Ebbw Vale ironworks in Wales, when zinciferous iron ores were smelted, and even into the 20th century these were still collected by the steel workers to cast into toys for their children, seemingly the latest and last chapter in a 2,000 year byeway in the story of zinc.

8. Zinc in India

8.1 Zinc Artefacts

The only early zinc artefacts that have been properly documented so far are the group of zinc vessels now in the Topkapi Saray Museum in Istanbul and a series of zinc coins from North West India.

The vessels were known in Iran as *tutya* and enjoyed a certain vogue in Iran and Turkey (Atil, et al., 1985, pp.29-30; Rogers and Ward, 1988, pp.132-3) (Fig. 8). Stylistically they were probably made in Eastern Iran or Afghanistan, although the metal itself is likely to have come from India. A non-destructive X-ray fluorescence surface analysis of vessel TKS 2/2873 performed by the author showed it to be of zinc with about a percent of lead and traces of silver. The vessels are encrusted with jewels and gold inlays, imitating shapes normally reserved for gold and jade vessels, suggesting these were prestige items restricted to court use. They now appear a dull grey and it would always have been difficult to polish without damaging the extensive insets and inlays. One suspects that they soon fell from

Fig. 8. Ornate vessels of zinc (TKS 2/2856), one of a group now in the Topkapi Saray Museum, Istanbul

Fig. 9. Zinc coins: Late Medieval *Jittals* from North West India Zinc coins from North West India, Series B, C & M Reg. 1892, 0207. 46-51. (A. Milton / BM)

favour as their impracticality became apparent and it is likely that their brief prestige was as a new material, akin to the zinc *baignoire de voyage* presented to the Emperor Napoleon by the Belgian zinc pioneer manufacturer, J J Daniel Dony in 1812.

A series of coins, now in the British Museum, believed to originate in the Punjab-Himichal Pradesh region of North West India, were analysed and found to be of almost pure zinc (Fig. 9) (Craddock, et al., 2015; Cribb, 2014). These coins, are closely related to issues in silver known as *jitals*, which were in circulation from the 12th to 14th centuries CE (Tye and Tye, 1995). The zinc coins are closest to those of the last three Kangra kings who ruled in the Himachal Pradesh region, although there is no evidence in their design to link them with any state authority, and it is possible that they were unofficial or religious coin-like tokens. Unfortunately the Kangra kings have no firm dates (see Cribb, 2014 for more detailed discussion on the problems of chronology), but it is most likely that the later kings ruled in the 14th century CE. The zinc coins are unlikely to date from very much later as the *jital*-like designs would not have been readily available after the 15th century. Thus, on balance, a 14th – 16th century date is most probable for the coins. Lead isotope analyses on these coins suggested a single source, not in the Aravallis but quite possibly further north in the North West of India.[9]

A possible production site was found by R C Dey, a geologist, who had collected many pieces of refractory from old mines and smelting places in the course of his travels, and these included zinc smelting retorts identical to 16th century retorts from Zawar at a small settlement known as Kwanu on the banks of the Tons River which divides the States of Himachal Pradesh and Uttatranchal in the far north west of India (Dey, 2008) (Figs. 1 and 10). Thus it seems that there

[9] The Dutch traveller, Abraham Rogerius, who spent many years travelling in South Asia in the 1630s, and who produced the standard work on Hinduism (Caland, 1915), wrote that taxes were paid to the temples in the Mughal Empire in part in *spiauter* (zinc), suggesting that zinc coins were quite prevalent in north India. There were also some low denomination coins of zinc minted by European traders in 18th century India, locally known as *bazarucos*, but with the zinc very likely coming from China (Yih and de Kreek, 1993).

Fig. 10. Another source of early zinc? Kwanu, a small settlement in the Dehradun District of Uttaranchal, on the Tons River

were other sites producing zinc in Medieval India and these coins are the earliest regular series of zinc artefacts known.

8.2 Early references to a Metal that should be Zinc

The early scientific literature contains several references to the production and use of zinc, and these have been collected together in Ray (1956). There is considerable uncertainty both of the dates of the various sources and also to the identity of the metal to which specific words refer. Fortunately the unique volatility of zinc, oxidising to give clouds of zinc oxide, makes it reasonably easy to identify where zinc is meant in the descriptions. Also, the medicinal use of the oxide as an antiseptic and salve, in India as well as in the Classical world (see above), means that there are references to it in medical as well as mineralogical contexts.

The earliest reference in the Sanskrit sources to a metal that could be zinc is found in the *Caraka Saṃhitā*, which is a medical treatise that was compiled in the early Buddhist period and which in its original form should date to around the mid first millennium BC (Rây, 1956, p.60). There, in chapter 26, it describes how a salve for treatment of infected eyes and open wounds, known as *puṣpānjana*, (the *–anjana* element denotes a salve), was to be made by burning a metal in air. The salve is surely zinc oxide, the familiar zinc ointment, and thus the metal to be burnt must be zinc. *Puṣpānjana* is also mentioned in the slightly later *Suśruta Saṃhitā*, and in the Medieval *Rasaratnasmuccaya* 109-112 (Ray, 1956, p.175). The mysterious word *tuttha* which could mean zinc or zinc oxide (see footnote 8).

The earliest dated reference to zinc from outside India was that made by the Iranian writer Abū Dulaf in his *al-risālat al-thāniya*, compiled around 950 CE (Allan, 1979, p.44) where he noted many kinds of tūtīyā which he stated come from the vapour of copper, except for the Indian *tūtīyā* which came from the vapour of tin.[10] One of the methods of preparing zinc oxide for medical usage in the Greek world as described by Dioscorides (see above) was by heating brass and collecting the vapour, and this would be the only indirect source available elsewhere, except of course in India, where a pure form, free of lead, and other harmful elements, could be had by burning zinc metal. Abū Dulaf's comment is interesting as showing that already by the 10th century CE metallic zinc was known, if only partially understood outside India itself, and that Indian *tūtīyā* was made by burning zinc metal, was already an item of international trade. The 11th century medical and mineralogical writer, Constantine the African, who had travelled extensively in the East before settling in Monte Cassino, in Italy, also described *spoduium* and *cadmea* as being products of India (*Opera* 1536, ps. 370 & 383), and in the 13th century, the scholar

[10] This statement has puzzled many, including Allan, as zinc oxide could not come from tin. The misapplication of the word tin to what was in reality zinc was a common failing by foreigners from Abu Dulaf in the 10th century through to no less an authority than Tod (1978 I, p.117, 223 etc) who in the 19th century described the workings at Zawar as tin mines. In Europe before the 19th century zinc was frequently confused with tin, and lacking any other name, was sometimes termed 'Indian tin'.

and theologian, Albert Magnus wrote of *tutty*, the white smoke that was collected from furnace flues, and the special, dark variety known as *Indian tutty* which may or may not have been zinc oxide or even the metal (Wychoff, 1967, p.250).[11]

The *Āīn-i Akbarī*, of Abū L-Faẓl Allamī written for the Mughal Emperor Akbar in the 16th century (Phillott, 1927, I, pp.40-2) not only correctly states that zinc is made from *tûtiyā* but makes the first reference to Zawar as its place of production.

> *Jast* [zinc], which according to the opinion of some, is *Rūḥ-i-tūtiyā* (that is, made from or originating from *tūtiyā*, zinc oxide), and resembles lead, is nowhere mentioned in the philosophical books, but there is a mine of it in Hindustan, in the territory of *Jālor*, which is a dependency of the bûba of Ājmīr.

8.3 The Smelting Operation (Craddock, et al., 1998b; 1998c; Craddock, 2017)

8.3.1 Early descriptions of the Production of Zinc

The descriptions of the zinc ores has been described above, and as already stated the most common ore available in India, certainly at Zawar, must have been sphalerite, unfortunately, the term *rasaka* for the zinc ore is usually interpreted as being calamine (smithsonite, the carbonate) in translations into English.

The earliest reference to the production of zinc by distillation is given in the *Rasaratnākara* which is believed to have been mainly compiled in the 6th to 8th centuries CE (see above) and is as follows:

> *Rasaka* (zinc ore) should be treated with *dhanyamia* (a fermented spirit similar to present day paddy) alkalis, and ghee (clarified butter) and then mixed with wool, lac, *harada* (or *hara*) (*Terminalia chebula*) *kencuā* (earthworms) and *suhāga* (borax). Upon heating it yields an extract which is white, shining like tin; of this there is no doubt. 31-32 (see also Ray, 1956, p.130)

The somewhat later *Rasārṇava* commenced its account by a description of the preparation of the ore:

> The *rasaka* powdered by the wise (*vaidya*) and put into a cloth bag is dipped into a container of women's urine for seven nights. The soaked powder is then treated with juices of yellow and red flowers (saffron, acacia, catechu, lac tree, *Terminalia chebula* and *dhāk* (*Butea frondosa*), and then treated repeatedly with alkaline, neutral and acidic solutions respectively. Then wool, lac, turmeric (*Curcuma roxob*), *harra* (*Terminalia chebula*), *kencuā* (earthworms), *suhaga* (borax) and *grahdhoom* (soot?) are mixed together and added to the treated ore. The product is then placed in the *mook mūṣa* (closed crucible, or more likely a retort) and heated strongly. The extract released on heating has a diamond-like shine which is undoubtedly zinc. VII 33-38 (Tripathi, 1978)

Ray (1956, p.138) translates this rather differently:

> *Extraction of Zinc from Calamine*:- *Rasaka* mixed with wool, lac, *Terminalia chebula* and borax and roasted in a covered crucible (retort) yields an essence of the appearance of tin; of this there is no doubt. VII. 37-38

The *Rasakalpa*, probably compiled in the twelfth or thirteenth century CE also gives a detailed description of how the ore is to be treated before smelting:

> *Extraction of Zinc from Calamine*:- Calamine, enclosed in fourfold pieces of cloth is heated in steam in a vessel for five months. Then it is powdered in a mortar and then mixed with treacle, soot etc. The mixture is then made into balls. These are enclosed in a crucible and strongly heated. The essence possessing the lustre of tin is thereby obtained. (Ray, 1956, p.157)

[11] Similarly, al-Khwarizmi, who wrote in the 10th century CE in Central Asia, noted various varieties of *tutty*, including the Indian which was white and precious, and a kind that was in the form of thin plates like palm leaves, recalling the plates of zinc oxide found at Zawar. Furthermore, the Indian form was artificial (Ryding, 1994).

Steaming seems a most unlikely treatment for a zinc ore. If it was the sulphide then the sulphate would most likely be produced, which would be very difficult to treat, if it was the silicate the treatment would ineffectual, and if it was the hydroxy carbonate, the treatment would be unnecessary.

The most detailed accounts of zinc smelting are contained in the *Rasaratna Samuccaya*, which was probably compiled in the late medieval period, between the fourteenth and sixteenth centuries CE. Ray believed it was compiled immediately prior to the arrival of the Portuguese. The work contains much earlier material, especially from the *Rasārṇava* and the *Rasaprakāśa Sudhākara*, the latter ascribed to Yasodhara, who is believed to have worked in the 12th or 13th century

The descriptions of the smelting of the zinc ores are as follows:

> *Extraction of Zinc*: Rub calamine with turmeric, the chebulic myrobalans, resin, the salts, soot, borax, and one-fourth its weight of *Semicarpus anacardium*, and the acid juices. Smear the inside of a tubular crucible with the above mixture and dry it in the sun and close its mouth with another inverted over it, and apply heat; when the flame issuing from the molten calamine changes from blue to white, the crucible is caught hold of by means of a pair of tongs and its mouth held downwards and it is thrown on the ground, care being taken not to break its tubular end. The essence possessing the lustre of tin, which is dropped, is collected for use. **157-61**. (Ray, 1956, p.171)

This was taken from the *Rasaprakāśa Sudhākara* of Yosadhara, and another contemporary account in the *Rasacintāmaṇi* of Madanantadeva, is similar, but with the added information that the process was judged to be complete as soon as the white fumes appeared (Ray, 1956, p.155). The blue flame would be made up in part from zinc vapour burning with a blue-green flame and carbon monoxide also burning with a blue flame. When this went white or white fumes appeared this would suggest that the conditions were no longer reducing and zinc was being turned into zinc oxide, and the process had better be terminated. Observing the flame colour and material issuing from the condenser end was the only way of determining what might be going on inside the retort, and similar comments that the process was judged complete when the flame or issue from the condenser turned from blue to white are to be found in European manuals on retort smelting (Percy, 1861, p.570; Lones, nd, p.101) and in descriptions of the traditional Chinese process (Craddock and Zhou, 2003).[12] From the instructions to pour the molten zinc from the vessel it would seem that the zinc metal collected inside the retort, which must have been heated with its neck pointing up. Other descriptions given in the *Rasaratnasamuccaya* have the neck pointing down and the zinc leaving the retort during the process as was the practice at Zawar.

> *Vṛntaka Crucible* (or retort):- Prepare a crucible in the shape of a *brinjāla* (aubergine) and put onto it a tube eight or twelve *aṅgulas* (inches) long, which opens out like a thorn apple flower (*Dāturā stramonium*), at one end. The tube should be hollow and have a circumference at the expanded end of eight *aṅgulas*. Such crucibles are known as *vṛantaka mūṣa* and are used for the distillation of *kharpar* (zinc ore) and other minerals. **23-24**. (see also Ray, 1956, p.191)

The actual process of *tiryakpatana yantram*, or distillation by descending, is described in Book 2 as follows:

> Take equal parts of lac, the bark of the papal tree, *hara*, myrobalans (*Terminalia cabula*), turmeric *haldi* (*Curcuma longa*), treacle, resin, rock salt, *suhāga* (borax), and *kharpara* (zinc ore). Bind them together and bake with cow's milk and *ghee* (clarified butter). Then make into balls and put into a *vṛantaka mūṣa* and heat strongly. The contents

[12] NB in the early stages of the process the flame would actually have been orange if the charge contained small quantities of common salt as often specified.

are then poured onto a slab of stone-the essence of *kharpara* of the beautiful appearance of tin is to be used. **163-4** (see also Ray, 1956, p.172)

Or, alternatively, having prepared the retort and its charge, as described above and fitted the condenser:

Dig a hole in the bottom of a *koṣṭhi* (the furnace) and place inside a water-filled vessel with a perforated plate or saucer over its mouth. Then fix the *vṛantaka mūṣa* in an inverted position over the perforated plate or saucer. Put charcoal of the *jubube* tree (*Ziziphus jububa*) over and around the *vṛantaka mūṣa* and heat strongly with the help of bellows. On heating the zinc extract descends and is collected in the vessel bottom. **165-68**. (see also Ray, 1956, p.172)

The quite detailed early descriptions of the ore charge for the zinc-smelting retorts (given below) are of some interest. It is important to realise that these descriptions were of laboratory operations that were either spagryrical or iatrochemical in their objectives. Thus some of the more exotic and expensive reagents, such as lac or turmeric, which also feature in many of the recipes given for other processes, and were almost certainly not used at Zawar. Similarly, the apparatus outlined in the early manuals have only one crucible or retort (Fig. 11). There was nothing

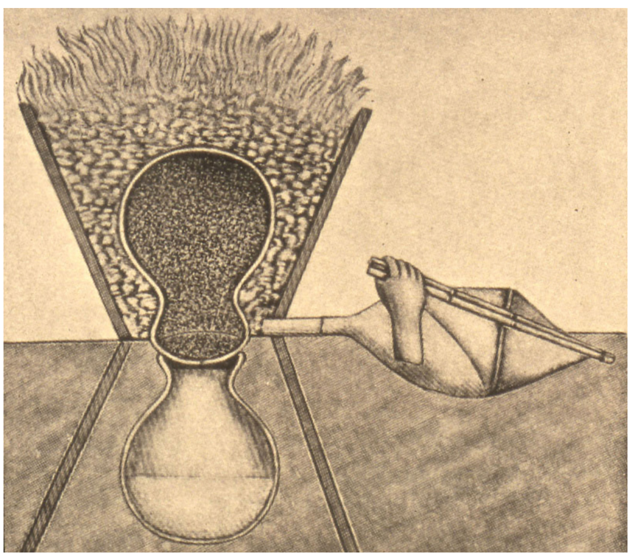

Fig. 11. Laboratory preparation: The distillation of zinc as envisaged from the Medieval Indian Iatro-chemical texts.

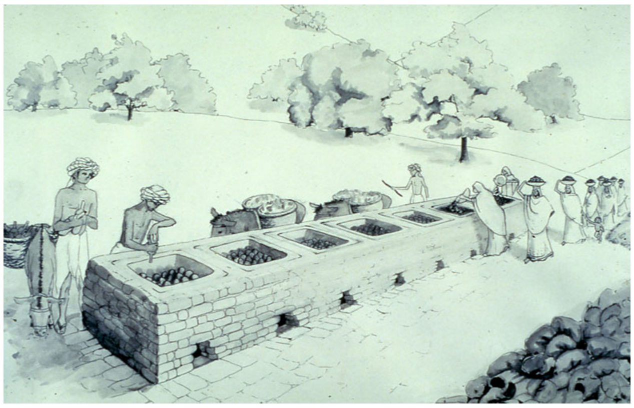

Fig. 12: Industrial production at Medieval Zawar. Typical furnace block holding 252 retorts together capable of producing approximately 70-80 kg of zinc per day. (B.R. Craddock)

in the contemporary literature to prepare us for the 252 retorts fired simultaneously in each *koṣṭhi* block at Zawar (Fig. 12).

8.4 Zinc Production at Zawar

8.4.1 History

The origins of zinc smelting at Zawar are not certain, zinc oxide was still being produced in the 7th century, and it is likely from a single early radiocarbon date that commercial production began some hundred years later. The first historic reference specifically to Zawar occurs in the reign of Maharana Lakha Singh (1382-1421 AD) (Hooja, 2006, p.331; Tod, 1978, I, pp.221-3). The territory in which Zawar lies is described as having been captured from the Bhils (the indigenous nomadic tribal people) and that silver and tin deposits had been discovered. Furthermore, mines had been opened, and silver, tin, copper, lead and antimony were being produced (Tod, 1978, I, ps. 117 & 223 etc). The tin was, of course, zinc and copper was probably produced in the general vicinity of Zawar, but there is no evidence of antimony mineralisation, possibly lead was meant. Certainly the major period of temple construction or possibly reconstruction at Zawar was in the 14th and 15th centuries (Kumar, 2017).

The Mughals under Akbar finally determined to end the independence of the Rajput kingdoms of Rajasthan and rapidly achieved this everywhere except at Mewar, including Zawar, where although defeated in battle resistance continued through the latter part of the 16th century and peace was not finally achieved until 1616. Through the 40 years of fighting, during which for some time Pratap Singh actually had a secret hideout in one of the ancient mines on Zawar Mala, it is likely that production was at least severely curtailed if not in total cessation. However the demand for zinc to make brass was still there in the rest of India and during this time Chinese imports carried in European vessels began to appear in Indian ports (see below) and possibly because Chinese zinc was cheaper, thereafter production at Zawar was much reduced. In the 18th century the Maharattas caused further disruption and production by the traditional process ceased by 1812 as recorded by Tod. In his history he gives the impression that after the *dosti* (friendship) with London peace and tranquillity was restored. However this was rather over optimistic and certainly through the 19th century the bhils and other nomads in the Zawar area were beyond government control and made any recommencement of mining in the area totally unrealistic (Pinhey, 1909; Hooja, 2006, p.803).

8.4.2 The process

At Zawar**,** the sphalerite ore was first roasted this to eliminate the sulphur, and mounds of white roasting debris surround the main smelting areas (Fig. 13).

Fig. 13. White heaps, Zawar. Where the ZnS ore was roasted to convert to ZnO, preparatory to charging to the retorts.

The roasted ore, still containing calcium and magnesium oxides and silica from the vein stuff, was made into small balls with sticky organic materials, very likely to have been cow dung, with charcoal and a little salt and placed in the clay retort. 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 1100^0 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 solely 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 and to create a central channel down which the zinc vapour could pass (Figs 14 & 15).

The furnace (*koṣṭhi*) was divided into two parts, the upper furnace chamber in the shape of a truncated pyramid (Figs. 16 & 17) which was separated from the lower square cool chamber beneath by perforated bricks (Fig 18). 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 these 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 six by

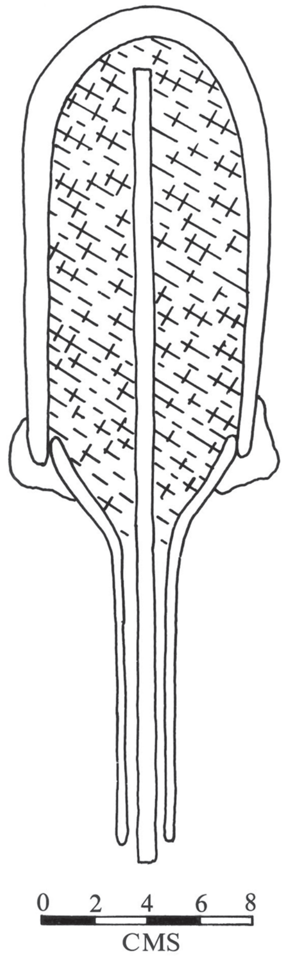

Fig. 14. Section through a retort with condenser luted in place and a stick inserted to hold the charge in place before charring and providing the central channel down which the zinc vapour could escape. (B.R. Craddock)

Fig. 15. Zawar: Retort broken in half showing the central channel down which the zinc vapour passed.

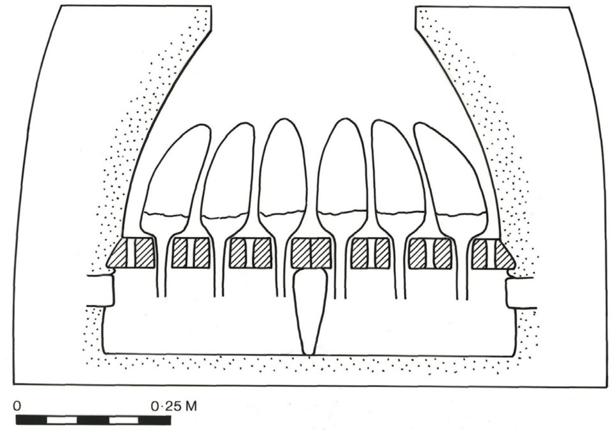

Fig. 16. Section through a typical furnace (B R Craddock)

Fig. 17. Zawar: Front view of furnace still bearing its last load of retorts.

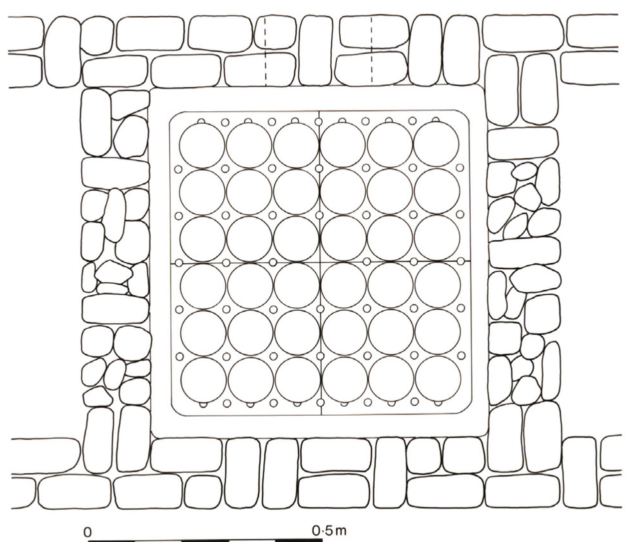

Fig. 18. Plan of a typical furnace at the perforated plate level. (B R Craddock)

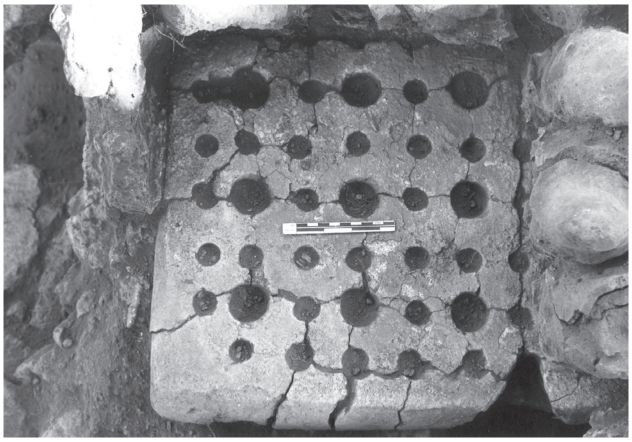

Fig. 19. Perforated plate, one of four in each furnace supporting the retorts.

six array in the furnace (Fig. 19). 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 the smelting times at the maximum temperature of about 1100^{0}C is estimated at between three to five hours, which accords well with memories of the last surviving smelters when interviewed in the mid19th century (Craddock, 2017).

The furnaces themselves were grouped in blocks, the earlier (14th-16th centuries CE) in blocks of seven and the later furnaces in blocks of three (16th-19th centuries CE). The process is estimated to have taken approximately 24 hours 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.

9. Zinc in China

The method developed by the Chinese is completely different from the Indian process (Craddock and Zhou, 2003; Zhou 2016). In this distinctive process the condensation and collection all take place within the retort itself (Fig. 20). This is the traditional Chinese method used for aqueous distillation, sometimes referred to as the Mongolian still (Needham, 1980, pp.62-74), and thus it seems most likely that the Chinese method for zinc production was a separate, indigenous development. 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.

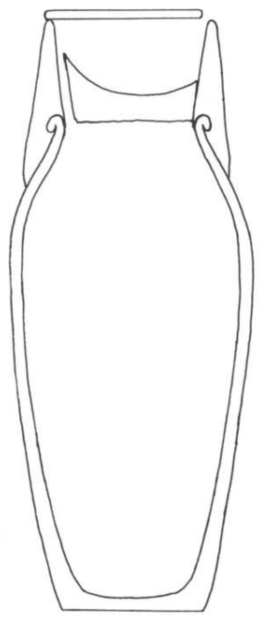

Fig. 20. Chinese Production: Section through a retort with internal condenser (from Zhou 2016)

9.1 History

It is believed that production of zinc developed out of the cementation process during the first half of the second millennium CE (Zhou, 2001). Recent excavations of major industrial production units in Chongqing, commensurate in scale to those at Zawar, are dated to the 16th century

(Fig. 21) (Liu, et al., 2007; Zhou, et al., 2012; Zhou, 2016). These belong to the developed industrial phase suggesting there are likely to be antecedents. Brass usage expanded enormously through the 16th century, and by the reign of the emperor Wan Li, 1573-1619, metallic zinc was definitely being produced on an industrial scale. This is attested both by the high zinc content of the contemporary brass *cash* coins, above what could be introduced by the direct process (Bowman, et al., 1989; Cowell, et al., 1993; Wang, et al., 2005), and by actual ingots of zinc being carried in Portuguese and Dutch vessels from the late 16th century (see below).

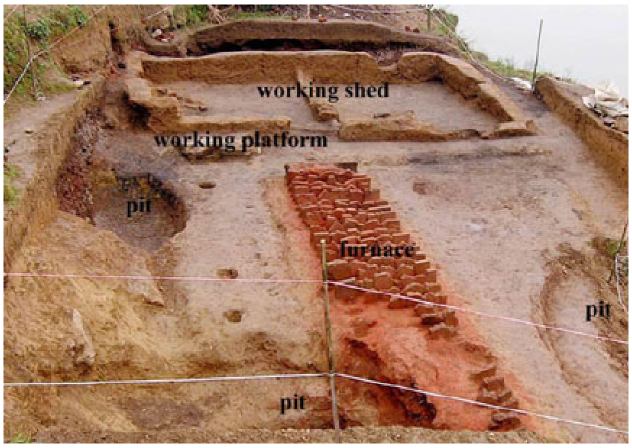

Fig. 21. Chinese Production: Foundation of furnace at Jiudaoguai, Fengdu, Chongqing, late 16th early 17th century CE. About 100 retorts were stacked vertically, in rows of three, supported by the low walls. (from Zhou 2016, Fig. 4.68)

9.2 Process

In the industrial production 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 CE (E-Tu Zen Sun and Shiou-Chuan Sun, 1966).

> Zinc [*wo-ch'ien*, lit. Japanese lead], a term of recent origin, does not appear in ancient books[13]. It is extracted from smithsonite, and is produced primarily in the T'ai-hang Mountains of Shansi, followed by Ching-chou [in Hupei] and Heng-chou [in Hunan]. Fill each earthen jar [retort] with ten catties (1 catty = approx. 0.6kg) of smithsonite, then seal tightly with mud, and let it dry slowly so as to prevent cracking when heated. Then pile a number of these jars in alternate layers with coal and charcoal briquettes, with kindling on the bottom layer for starting the fire. When the jars become red-hot, the smithsonite will melt into a mass. When cooled, the jars are broken open and the substance thus obtained is zinc, with a twenty percent loss in volume. This metal is easily burnt off by fire if not mixed with copper. Because it is similar to lead, yet more fierce in nature, it is called "Japanese lead".

The process was clearly carried on inside the vessel (that is with an internal condenser) but the observation that the lid was sealed tightly must be incorrect as without some outlet the sealed vessel would have burst upon heating. Also there is no mention of a reducing agent, coal or charcoal, to reduce the zinc ore inside the retort.

Based on the excavated furnaces, and records made of the traditional process in the 20th centuries (Liu, et al., 2007) and their scientific examination (Zhou, et al., 2012; Zhou, 2016), the process can be described in detail. The mixture of ore and special low sulphur coal was charged to the retorts and a layer of fine grained furnace ash with a little slurry placed on top of it. This was then carefully pressed down with a stone or iron hammer and a depression was created on the top. An iron plate was inserted to one side of the ashes on the top to keep a passage open through which the zinc vapour would pass to the top of the retort where it condensed. Clay was coiled around the rim of the retort to build up a pocket about 10cm tall. Finally an iron lid was placed on top of the pocket and sealed with more mud, leaving only a small hole to act as a gas passage during the smelting process. The zinc condensed on the underside of the lid and dripped down into the collecting pocket.

[13] NB Abū L-Faẓl's very similar comments made in India some 40 years previously (page 17)

Based on the dimensions of the excavated hearths and retorts, there could have been about 60-90 retorts on a platform. The gaps between the hearth walls and the top of the retorts were filled with suitable-sized slag lumps and mud. This sealing was of importance to keep the temperature of the pockets above the retorts at a lower level than that of the retort during the smelting process and also to physically stabilise the retort. During the smelt the temperature of the part of the retort where the reaction took place would have been about 1200°C but the temperature in the pocket would have been about 800°C, essential for the rapid condensation of zinc vapour. It is estimated that it would have taken about 20 hours for the materials in the retorts to react completely after the lid was placed on the pocket. In practice the experience of craftsmen would have been necessary to decide when the reaction was complete. This was done by observing the colour of the small flame, emitted by the burning carbon monoxide through the small hole in the iron lids of the retorts. After cooling the retorts for about 5-6 hours the zinc ingots could be taken out of the pockets. Zhou (2016, pp.77-8) estimated that a furnace block could produce about 60 kg of zinc per day.

The process continued with only minor changes up to the 1970s attracting the usual pejorative comments from Europeans and Americans such as Ingalls (1936):

> The Chinese in remote places still produce small quantities of zinc. I have seen photographs of their furnaces; or pots, for they hardly deserve the dignity of being called furnaces. I imagine that they are the same that were used centuries ago, for I cannot conceive of anything more primitive.

As described by Xu (1998) the furnaces 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 (Fig. 22). 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.

Fig. 22. Chinese Production mid 20th century. Removing a retort from the furnace in the Magu District of Guizhou. Note the retorts are in threes, as with the earlier furnaces (cf Fig. 22). (Li, 1998)

Thereafter the traditional process underwent major changes, enabling 50 - 60 retorts to be fired together in one chamber, with the fire separate from the retort chamber (Figs 23, 24 & 25) (Craddock and Zhou, 2003).

10. Zinc in International trade in the Post Medieval world

From the end of the 15th century Portuguese ships began trading directly first with South Asia and then with South East Asia and the Far East after 1511. The Portuguese were joined by the Dutch, Spanish, English and French from the later 16th century, and it seems likely that zinc formed part of the early cargoes. The experiences

Fig. 23. Evolved traditional Chinese process. Two retort chambers with their fires now separate and central chimneys. Huize District, Yunnan1994/5 (Craddock and Zhou 2003)

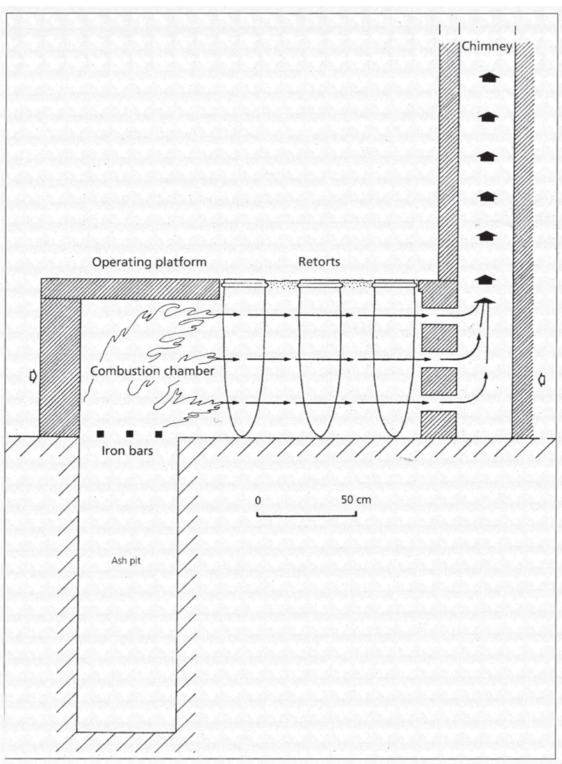

Fig. 24. Section of the 20th century Chinese traditional process shown in Fig.23.(B R Craddock)

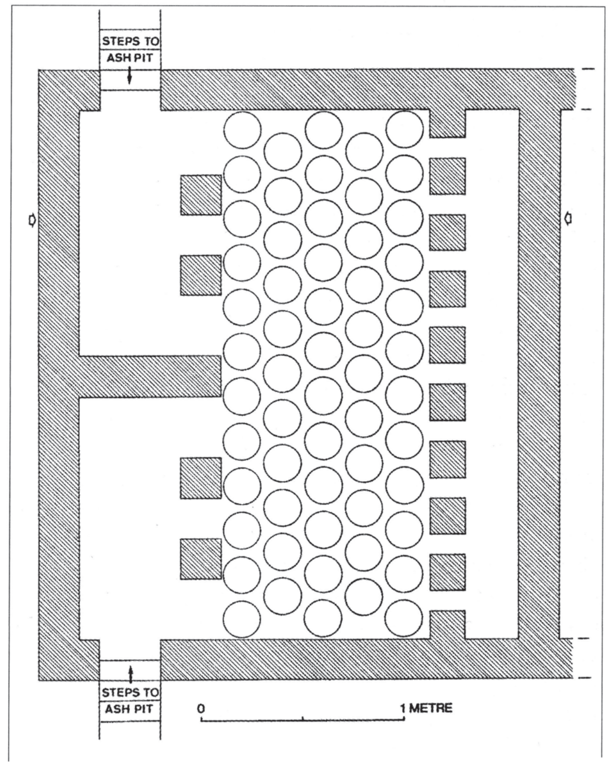

Fig.25. Plan across one side of the20th century Chinese traditional furnace depicted in Fig. 23. (B R Craddock)

of the Indian and Chinese zinc industries in international trade were to be very different.

Unfortunately details of the cargoes for the 16th century are sparse and there is the familiar problem of nomenclature.[14] Both the Portuguese and English trading companies established trading centres in north west India, the Portuguese at Diu and the English at Surat (Fig. 1) both in north west India and would have been convenient for Zawar. There are two early reports of Portuguese vessels carrying metal cargoes that could be zinc.

[14] As zinc was almost unknown in Europe there was a continuing confusion over what exactly it was and what it was called, leading in turn to confusion over the identification of some metals (see Bonnin, 1924 for the best attempt at clarification). When dealing with East Asia the Dutch mainly called the metal variants on *spelter*; the English variants on *tutenag* (finally degenerating into terms such as 'tooth and egg metal' by the early 19th century, as recorded by Bonnin, 1924, p. 52). When dealing with South Asia the Portuguese often used variants of the word *calaem*, but there was and still is considerable confusion whether *calaem* and its derivatives meant tin, zinc or any white metal alloy. Forbes (1971, p.282) suggested that the word derived from the Arabic word *kala'i*, that is 'coming from Kedah (Qualah) in Malacca, and should be interpreted as tin. Quite often a metal is described as 'Indian tin' or 'tin from India', which as tin was only ever produced in tiny quantities in South Asia, and formed parts of the cargoes imported into India from the earliest days, presumably the metal was actually zinc (see footnote 8). However, there is the possibility that at least some of the *calaem* bought in India in the 16th century, really was tin, but had come from South East Asia.

An Italian, Antonio Bavarin, writing from London on October 26th 1513, stated that he has received letters from Lisbon advising of the arrival of three spice vessels, which also carried 'some 400 pieces of tin which if good will be very detrimental to the English, for they (the Portuguese) say they can have as much as please.' This could conceivably have been tin from South East Asia, Mallaca having been captured by the Portuguese in 1511, but at this early date it seems far more likely that the ships had returned from India, and thus zinc is a more likely interpretation (see footnote 10).

The second is a record of a Portuguese vessel loaded with 21 *quintals* (960 kg) of *kalaem* (see footnote 14) at Cambay, at the head of the Gulf of Khambhat (Cambay) in Gujarat (Fig. 1), sailing for Sofala in Abyssina in 1519 (Godhino, 1991, I, p.204). Africa might seem an unlikely destination, but country trade within the Indian Ocean and beyond was always an important component of European trade, and a century later Antonio Gomes' 1648 account of the Kingdom of Monomotapa (centred on modern Zimbabwe and Mozambique) stated that:

> There is a great deal of copper...they make an alloy of this copper with a metal like tin, but somewhat different, which, if it were reckoned in carats would be better than tin, and which in India is called *calaim* (moutane) by the Kaffirs of Goa.

Analyses of metal artefacts belonging to the historic period from East Africa has confirmed the presence of brass, together with more specifically Indian metals, notably crucible steel (Kusimba, et al., 1994).

With the further eastward exploration of the Portuguese, into the waters of South East Asia after 1511, followed by the Spaniards, coming west from the Americas and establishing themselves in the Philippines, the markets and products of the Far East began to be exploited. The Portuguese and the Spaniards were soon joined by the Dutch who already by the end of the 16th century were the dominant European traders in the Far East and were to remain so until the demise of the Dutch East India Company in the 1790's. Amongst the products from South East Asia and the Far East were tin from Malaya and Thailand and zinc from China. Although brass did not become popular in China until the 16th century within a short space of time, the end of the century at the latest, zinc metal was a major export commodity in the international maritime trade (Bonnin, 1924; Souza, 1986; 1991; Zhou, 2016, pps. 13-4 & 126-8). The early history of the international trade in Chinese zinc is uncertain, as indeed are the dates of the commencement of industrial zinc production in China itself (see above p.00). Almost the earliest hard evidence are zinc ingots from China in European vessels that were captured or sank. For example it is recorded that the Dutch captured a cargo of ingots, referred to as being of 'Indian tin' from a Portuguese vessel in the Malacca Straits. Some of these were studied by the Dutch scientist Libvarius in 1596, and identified as being of zinc (Partington, 1961, p.259), and which can only have originated in China. Zinc ingots have also been recovered from vessels of the Dutch East India Company, lost en route to Europe, such as the VOC *Maurice*, wrecked in 1609 off the coast of West Africa, and the *Witte Leeuw*, wrecked in 1613 off St Helena (Craddock and Hook, 1997).

The principal items exported from India were spices and textiles and the principal imports were metals (Prakash, 1985). Gold and silver were required in payment for the exports, but non-ferrous metals generally metals also seem to have found a ready market almost from the inception of trading (Craddock, 2013). What is very surprising is that India, the home of the first zinc industry, imported Chinese zinc on a considerable scale from the early 17th century at the latest (Craddock 2009). Through the 17th and 18th centuries this trade was quite substantial, thus for example in the late 17th and early 18th century approximately 40 tons per annum were imported into Bengal at Calcutta by the Dutch, and this was not their only port of entry into South Asia (Prakash, 1985, pp.161-2). The trade was not always necessarily direct, thus there is a record of 1644 that 'they export from Cochin (in the south of India) to Orissa (in the north east) *callaym, tutenaga*, wares of China and Portugal' (Bonnin,1924). The appearance of Chinese zinc on the international market and in India at the end of the 16th century could reflect the considerable disruption that must have taken place at Zawar during the suppression of Mewar by the Mughal emperor Akbar through the latter part of the 16th century (see above).

However, as our excavations have shown, and the historic record relates, zinc production at Zawar resumed in the 17th and 18th centuries, although probably on a reduced scale (see above), and some Indian zinc continued to be exported (Craddock 2009), as Watson (1796, p.28) related:

> The eastern Indians (i.e. from South Asia) have long since been in possession of the method of extracting pure zinc from the ore; at least in the course of the last century this metal has been brought from thence to Europe. Jungius mentions the importation of zinc from India in 1647 (in his *De Mineralibus*); a metal of this kind under the name of Tutenag is still brought from thence.

The import of zinc into Europe is imperfectly studied, even for the 18th and early 19th centuries when at least the identity of the metal is reasonably certain. It is not clear how much was still coming from India and how much from China. In 1744 a Swedish vessel sank in Gothenburg harbour, laden with Chinese zinc ingots, some of which have been recovered and studied (Carsus, 1959). Malachy Postelthwayt wrote in 1751 in *The Universal Dictionary of Trade and Commerce* that:

> Our artificiers have long been acquanted with zink under the name spelter... We have much brought also from the *East Indies* under the name of tutenage, yet nobody ever knew from what or how it was produced there... There is great reason to believe that all the zink or tutenage brought from the *East Indies* is produced from Calamine: and we have now on foot at home a work established by the great discoverer of this ore, which will probably very soon make it unnecessary to bring any more zink from elsewhere into England...

Postelthwayt's comments on 'the discoverer of this (calamine) ore' must refer to the establishment of a true zinc distillation industry, based on the Indian process, at Bristol by William Champion in 1742 (Day, 1973). The process as adapted by Champion was not very successful, but did attract considerable interest in Europe (Day, 1984). By the end of the 18th century several much more efficient processes had been developed (Almond, 1998), notably the Dony, horizontal retort process, that was to continue through well into the 20th century (Dutrizac, 1989). The rise of the European industry challenged and finally terminated the Asian international export trade in zinc

The records of zinc imported into England from the 1760s state that the metal, averaging about 40 tons per annum, was coming from East India, declining until in 1779 only about 3 tons were imported. East India could just refer to the East India Company, and thus include Chinese zinc, although the decline and cessation would fit very well with what is known of the decline at Zawar (see above).

In terms of costs, Zhou (2016) showed that the Chinese producers had three distinct advantages over their Indian counterparts. The ore used was the carbonate, smithsonite, that only required moderate calcining. This was normally carried out in the open retorts as the first stage of the process before reduction, rather than the full separate roasting stage to treat the sulphide ores, and thus the losses of zinc were minimised. Secondly, the Chinese were able to use mineral coal, not only ordinary coal to heat the retorts from outside, but also special low sulphur coal within the retorts acting as the reductant. Finally the traditional Chinese retorts were re-usable (Typically seven times in the late 20th century, Craddock and Zhou, 2003). The size of the 16th century Indian and Chinese retorts are similar and thus the yield per retort is likely to have been broadly the same. Both the Indian and Chinese fired many retorts together and thus the overall yield per furnace block is also likely to have been broadly similar.

Only relatively small amounts of zinc seem to have been sent to Europe, where it was an expensive and exotic commodity, arousing considerable academic interest as to its nature, and what to do with it.[15] Matters were different in Asia. Ships sailed to China from Europe with lead as the cheap ballast cargo, where it was unloaded and replaced with zinc as the cheap durable cargo for the voyage to India (Souza, 1991). It would no doubt have surprised the European savants to learn that this technically sophisticated material was cheap and common place in the East.

In 1813 Milburn's *Oriental Commerce* noted that:

> The Dutch used to import large quantities into Holland (the VOC ceased to trade in 1799), on an average of 7 years, 1785 to 1791, 202,757 lbs. (approximately 90 metric tons) per annum.

After the 18th century zinc was no longer being sent to Europe, but there was still a considerable country trade to India, continuing well into the 19th century (Cranmer-Byng, 1962). In more detail Sir T. Dick Lauder wrote in the *Edinburgh Journal* **XV** in 1820 that:

> Tutenag is an article of very extensive trade between India and China; and my friend informs me that it is sent from China slabs, of which he had occasion to buy and sell many thousands. The slabs are about eight or nine inches long, by about five and a half wide, and about five-eighths thick.[16] It is employed by the natives of India as an alloy for copper to make brass for their domestic utensils.

However the supremacy of Chinese zinc in international trade was rapidly drawing to a close, thus in 1834 John Holland in his *Treatise on Manufactures in Metal* quotes Dick Lauder's remarks and continued:

> Such was the description of this celebrated matal (*sic*) about 1820 until which period the interest of the importers had invested it with as much mystry (*sic*) as possible: in that year however the British free traders introduced German spelter into India to compete with the Chinese metal, the similar composition of which they had discovered. In 1826, the importation of tutanag from China into Calcutta ceased: and is now totally superseded throughout India by spelter. Of this latter commodity there was, according to M'Culloch, exported from British ports, at an average of the three years ending with 1828 126,329 cwt (about 6,000 tons) of the declared value of £95,000 (i.e. £15 a ton) besides the quantities furnished by Hamburg, Rotterdam, Antwerp and other Continental ports.

Fig. 26. Chinese zinc ingot part of the cargo of the EIC *Diana*, wrecked in the Malacca Strait, enroute to Calcutta in 1812. (A. Milton / BM)

[15] European curiosity was aroused by this strange metal, *caleum* or *calim*, encountered in the East. For example De Laval in 1679 noted that *calim* was whiter than tin but more beautiful, and that the metal was highly prized throughout India (quoted in Partington, 1961, p.109).
In Europe it was commonly regarded as a 'half metal' until the 19th century.

[16] As exemplified by the EIC *Diana* which sank on her way to Calcutta laden with Chinese zinc in 1812 (Fig. 26) (Ball, 1995).

11. Overview

> Though the value of the old Indian alchemists and their modern commentators is very doubtful it seems that zinc was prepared by Indian chemists since the 12th century, but that this remained a laboratory experiment and was never applied to industrial production (Forbes, 1964, p.281)

Brass, and latterly zinc usage began in the broad region stretching from Anatolia through to North West India. A notable feature of this region is the absence of viable sources of tin. This is in contrast with other regions such as central Europe, Ireland, southern India, China and South East Asia which either had local tin sources or easy access to tin and where bronze remained as the usual copper alloy for much longer.

The production of zinc probably began on a laboratory scale by the iatro-chemists in India in the latter part of the first millennium BCE and beginning of the first millennium CE. The reason for doing so was very likely for the production of a lead-free zinc oxide by combustion of the zinc metal for pharmaceutical use. The inspiration for the method of distillation was very likely to have been based on the existing, and much simpler technology for the production of mercury by a form of *tiryakpatana yantram*, or distillation by descending.[17] The great achievement of the Indian chemists and entrepreneurs was to transform this laboratory procedure into an industrial process capable of producing zinc metal on a scale and at a cost where speltering could compete with the existing methods of making brass. It would seem likely that the driving force behind the development of large scale zinc production was the need to develop a more efficient way of producing brass. Both in India and in China the industrial production of zinc was almost exclusively for the manufacture of brass, with minor amounts still used for pharmaceutical use.

At Zawar there are large numbers of furnace blocks each of which held hundreds of retorts fired simultaneously. Although the principle of distillation was still *tiryakpatana yantram*, as described in the iatrochemist's texts, the form of apparatus is totally different. The *koṣṭhi* could be based on the furnaces used in the production of saltpetre by concentration and crystallisation from aqueous solution, or probably from the furnaces already in use for the production of brass.

Initially at Zawar the individual refractory components comprising the process, perforated plates, condensers, etc were hand-made and seems likely that each furnace block was independent. However by the 14th century this had significantly changed and now although the principle and form of the furnaces were the same the refractory components were formed in moulds to very regular dimensions, strongly suggesting that they were all made in central workshops to a standard pattern. Similarly the medieval opencast trench mines for zinc ore are enormous and realistically could only have been worked satisfactorily under a single authority. In India as elsewhere mineral rights were normally held by the ruling authority. Zawar was also a noted centre of the Jains and many of the temples were built by them.

The Jains have a long tradition of merchant and entrepreneurial endeavour. Thus it is possible to envisage the technical development of the laboratory procedure into an industrial process was undertaken by the Jain community at Zawar, with the overall control and encouragement from the ruling administration of Maharana Lakha Singh (1382-1421 CE).

11.1 China

The organisation and administration of the industry in China has been discussed by Zhou (2016, pp.108-10). During the period that the zinc producers studied by her were in operation (16th to 18th century) the overall control would have been the Ming Dynasty and its appointees. In the

[17] *Rasaka*, the medieval Hindu term for zinc ore, derives from *rasa*, the Tantric word for mercury.

Early Ming Period (16th century) state control was likely to have been fairly tight with the operations run directly by the state often using impressed labour. By the Mid Ming period control had slackened and with the development of a more commercial economy there was more opportunity for private enterprise and this developed still further in the Late Ming period with the operations run privately, with the furnace blocks run singly or in groups. However the mineral resources would have still been owned at least theoretically by the state and a hefty tax was still imposed. Also as Zhou (2016) points out the furnace blocks seem very similar suggests that even if independent they relied on central sources of ore, fuel and also probably components such as the retorts, as at Zawar. By the beginning of the 20th century with the breakdown of central authority the operations were almost exclusively private concerns.

12. Conclusion

The technical achievements of both India and to a lesser extent of China, have long been or ignored or belittled (as illustrated by the quote from the eminent historian of technology, R J Forbes, at the head of this section). Nowhere is this truer than in the development of chemical industry. This is usually seen as a strictly European phenomenon occurring in the 18th century. This was when an entrepreneurial class, typically belonging to independent protestant Christian groups such as the Quakers, with some scientific interest and knowledge was able to attract sufficient financial support to allow development to begin and flourish. It would seem very probable that exactly the same cultural and entrepreneurial climate existed in India a good half millennia earlier, except that the Quakers were Jains and the bankers were maharajahs.

Bibliography

Allan, J W. Persian Metal Technology, *700 – 1300 AD*, Ithaca Press. London, 1979.

Almond, J K. Zinc Production Technology 1801-1950 A Review. in Craddock (ed.), 1998, pp. 159-228.

Atil, E; Chase, W T and Jett, P. Islamic Metalwork in the Freer Gallery of Art, Smithsonian Institution, Washington, D.C. 1985.

Ball, D. The Diana Adventure, Malaysian Historical Salvors, Kuala Lumpur & Kemper, Gronigen, 1995.

Bandy, M C and Bandy, J A. De Natura Fossilium, Dover, New York, 2004.

Bayley, J. The production of brass in antiquity with particular reference to Roman Britain. in Craddock (ed.), 1998, pp. 7-25.

Bayley, J. and Butcher, S. Roman Brooches in Britain: A Technological and typological Study, Society of Antiquaries of London, London, 2004.

Bedore, C and Dixon, C. New discoveries in an old collection, *Context* 13 (1998): 3-4.

Bonnin, A Tutenag and Paktong; With Notes on Other Alloys in Domestic Use During the Eighteenth Century, Oxford University Press. Oxford, 1924.

Bowman, S G E, Cowell, M R and Cribb, J. Two thousand years of Coinage in China: An analytical study, *Journal of the Historical Metallurgy Society* 23 1. (1989): 25-30.

Burnett, A M; Craddock, P T and Preston, K. New Light on the Origins of *orichalcum*, in, T Hackens and R Weiller (eds.), Proceedings of the 9th International Congress of Numismatists, Association Internationale des Numismatists Professionels. Publication 6, 1982. pp. 263-68.

Caland, W. (ed.) Abraham Rogerius: De open-deure tot het verbogen Heyendom, M. Nijhoff, Gravenhage, 1915.

Caley, E R. Orichalcum and Related Ancient Alloys, Numismatic Notes and Monographs 151. The American Numismatic Society, New York, 1964.

Cameron, H.K. Technical aspects of monumental brasses, *The Archaeological Journal* 131 (1974): 215-37.

Caple, C. Factors in the production of medieval and post-medieval brass pins, in D R Hook and D R M Gaimster (eds.) Trade and Discovery: The Scientific Study of Artefacts from Post-Medieval Europe and Beyond. British Museum Occasional Paper 109, London,1995, pp.221-34.

Carradice, I and Cowell, M. Minting of Roman Imperial Bronze Coins for circulation in the East: Vespasian to Trajan, *Numismatic Chronicle* 147(1987): 26-50.

Carsus, H D. Historical Background, in C H Mathewson (ed.), Zinc, American Chemical Society Monograph, Rheinhold, New York, 1959, pp. 1-8.

Cowell, M R; Cribb, J; Bowman, G G E; and Shashoua, Y. The Chinese cash: composition and production, in Metallurgy and Numismatics 3. M.M. Archibald and M.R. Cowell (eds.). Royal Numismatic Society Special Publication 24, London. 1993, pp.185-98.

Craddock, P T. The Composition of the Copper Alloys used by the Greek, Etruscan and Roman Civilisations 3: The Origins and Early Use of Brass, *Journal of Archaeological Science* **5** 1(1978): 1-16.

Craddock, P T. *Early Metal Mining and Production*, Edinburgh University Press, Edinburgh. 1995.

Craddock, P T. (ed.) 2000 Years of Zinc and Brass, 2nd ed. British Museum Occasional Paper 50, London, 1998.

Craddock, P T. Zinc in Classical Antiquity, in Craddock (ed.) 1998, pp.1-6.

Craddock, P T. Some Analyses of Medieval Monumental Brasses, *Transactions of the Monumental Brass Society*,16.4 (2000/1): 315-26.

Craddock, P T. Conservative metal alloying traditions in the Migration Period, in Archaeometallurgy in the Central Europe III, *Acta Metallurgica Slovaca*, 7(2001): 175-81.

Craddock, PT. Perceptions and Reality: The Fall and Rise of the Indian Mining and Metal Industry, in T.L. Kienlin and B W Roberts (eds.), Metals and Societies, Rudolf Habelt GMBH, Bonn, 2009, pp.453-64.

Craddock, P T. Two Millennia of the Sea-bourne Metals Trade with India, *Indian Journal of History of Science* 48.1(2013): 1-37.

Craddock, P T. *Early Metallurgy in India*, Archetype, London, 2017.

Craddock, P T; Burnett, A M and Preston, K. Hellenistic copper-base coinage and the origins of brass, in W A Oddy (ed.), Scientific Studies in Numismatics, British Museum Occasional Paper 18, London, 1980, pp.53-64.

Craddock, PT and Lambert, J. The composition of the trappings, appendix in Jenkins, A. A group of silvered-bronze horse trappings from Xanten (*Castra Vetera*), *Britannia* 15 (1985): 141-64.

Craddock, P T and Hook, D R. The British Museum collection of metal ingots from dated wrecks, in M Redknap (ed.), Artefacts from Wrecks, Oxbow Monograph, Oxford. 1997, pp.143-54.

Craddock, P T; La Niece S C and Hook, D R. Brass in the Medieval Islamic world, in Craddock (ed.) 1998a. pp. 73-114.

Craddock, P T; Freestone, I C; Middleton, A; Gurjar, L K and Willies, L. Zinc in India, in Craddock (ed.) 1998b, pp.27-72.

Craddock, P T; Freestone, I C; Willies, L; Paliwal, H V; Gurjar, L K; and Hegde, K T M. Ancient Industry of Lead, Silver and Zinc in Rajasthan, in V Tripathi (ed.), *Archaeometallurgy in India*, Sharada Publishing House, Delhi. 1998c, pp.108-33.

Craddock, P T and Eckstein, K. Production of Brass in Antiquity by Direct Reduction, in P.T. Craddock and J. Lang (eds.), *Mining and Metal Production through the Ages*, British Museum Press, London, 2003, pp.216-30.

Craddock, P T and Zhou, W. Traditional Zinc Production in Modern China, in P T Craddock and J Lang (eds.), *Mining and Metal Production through the Ages*, British Museum Press, London, 2003, pp.267-92.

Craddock, P; Cartwright, C; Eckstein, K; Freestone, I; Gurjar, L; Hook, D; Middleton, A and Willies, L. Simple sophistication: Mauryan silver production in North West India, *British Museum Technical Bulletin,* 7(2013): 79-93.

Craddock, P T; Cribb, J; Gale, N H and Gurjar, L. Sources of zinc in early India: The evidence of numismatics, trade and lead isotope analysis, in S Srinivasan, S Ranganathan and A. Giumlia-Mair (eds.), *Metals and Civilisation*, National Institute of Advanced Studies, Bangalore, 2015, pp. 174-84.

Cranmer-Byng, J L. (ed.) *An Embassy to China: Being the Journal kept by Lord Macartney* 1793-4, Longmans Green. London, 1962.

Cribb, J. Indian zinc coins, *Journal of the Asiatic Numismatics Society*, 219 (2014): 321-31.

Dash, B and Kashyap, L. (ed. and tr.) *Iatro-Chemistry of Āyurveda (Rasa Śāstra)*, Concept Publishing Co., New Delhi, 1994.

Day, J. *Bristol Brass*, David and Charles, Newton Abbot, Devon, 1973.

Day, J. The Continental Origins of Bristol Brass, *Industrial Archaeology Review*, 7.1(1984): 32-55.

Dey, R C. Ancient Smelting Devices (Retorts) from Different Parts of India, *Journal of the Geological Society of India,*72 (2008): 527-32.

Dungworth, D. Caley's 'zinc decline' reconsidered, *The Numismatic Chronicle*, 156 (1996): 228-34.

Dungworth, D. Roman Copper Alloys: Analysis of Artefacts from Northern Britain, *Journal of Archaeological Science,* 24 (1997): 901-10.

Dutrizac, J E. The end of horizontal zinc retorting in the United States, *CIM Bulletin* 76 (850) (February 1989): 99-101.

E-tu-Zen Sun and Shiou-Chuan Sun (tr. and ed.) *T'ien-kung K'ai-Wu*: *Chinese Technology in the 17th century*, by *Sung Ying-Hsing,* Pennsylvania State University Press, Philadelphia, 1966.

Falk, H. Silver, Lead and Zinc in Early Indian literature, *South Asian Studies,* 7(1991): 111-17.

Farnsworth, M; Smith, C S and Rodda, J L. Metallographic Examination of a Sample of Metallic Zinc from Ancient Athens, *Hesperia* (Supplement **8**) (1949): 126-29.

Forbes, R J. *Studies in Ancient Technology* VII*,* E J Brill, Leiden, 1964.

Forbes, R J. *Studies in Ancient Technology* VIII, 2nd ed. E J Brill, Leiden, 1971.

Furger, A R and Riederer, J. *Aes* und *Aurichalcum*. Empirische Beurteilungskriterien für Kuper-legierungen und metallanalytische Untersuchungen an Halbfabrikaten und Abfällen aus metallverarbeitenden Werkstätten in Augusta Raurica, *Jahresberichte aus Augst und Kaiseraugst* 16 (1995): 115-80.

Godhino, V M. Os Descobrimentos e a Economia Mundial, 4 vols. Presença, Lisbon, 1991.

González, A R. Pre-Columbian Metallurgy of Northwest Argentina: Historical Development and Cultural Process, in E.P. Benson (ed.), *Pre-Columbian Metallurgy of South America,* Dumbarton Oaks, Washington DC,1979, pp.133-202.

Grant, M. From Imperium to Auctorias, Cambridge University Press, Cambridge, 1946.

Gunther, R T. (ed.) *The Greek Herbal of Dioscorides,* John Goodyer's translation of 1655. Oxford University Press, Oxford, 1934.

Haedecke, K. Gleichwichtsverhaeltnisse bei der Messingherstellung nach dem Galmeiverfahren, *Erzmetall,* 26.5 (1973): 229-33.

Halleux, R. L'orichalque et le laiton, *Antiquite Classique* 42 (1973): 64-81.

Hawthorne J G and Smith, C S (tr. and ed.) *On Divers Arts*: *The Treatise of Theophilus*, University of Chicago Press, Chicago, 1963.

Hooja, R. *A History of Rajasthan*, Rupa, New Delhi, 2006.

Hoover, H C and Hoover, L H. (tr. and ed.) *Agricola*: *De re Metallica*, *The Mining Magazine,* London, 1912. (reprinted 1950, Dover, New York).

Hughes, M J; Lang, J R S; Leese, M N and Curtis, J E. The evidence of scientific analysis: A case study of the Nimrud bowls, in J E Curtis (ed.), *Bronze-working Centres of Western Asia*, Kegan Paul, London, 1988, pp.311-16.

Ingalls, W R. History of the Metallurgy of Zinc, Chapter I of *Metallurgy of Lead and Zinc, Transactions of the American Institute of Mining and Metallurgical Engineers*, 121(1936) 339-73.

Istenic, J and Smit, Z. The beginning of the use of brass in Europe with particular reference to the southeastern Alpine region, in La Niece, et al. (eds.) 2007, pp.140-47.

Jackson, R and Craddock, PT. The Ribchester Hoard: A descriptive and Technical Study, in B. Rafferty (ed), *Sites and Sights of the Iron Age*, Oxbow, 1995, pp. 75-102.

Jones, H L. (trans.) *Strabo*: *Geography*, VII. The Loeb Classical Library, Harvard University Press, Cambridge, Ma,1928.

Kangle, R P. (trans. and ed.) *The Kauṭilīya Arthaśāstra*, 3 vols. Bombay University Press, Bombay, 1965, 1969 & 1972.

Kenoyer, J M and Miller, H M-L. Metal Technologies of the Indus Valley Tradition in Pakistan and Western India, in V C Pigott (ed.) *The Archaeometallurgy of the Asian Old World*, MASCA Research Paper 16, University of Pennsylvania Museum, Philadelphia, 1999, pp.107-51.

Kharakwal, J S. *Indian Zinc Technology in a Global Perspective,* Pentagon Press and Infinity Foundation Series, New Delhi, 2011.

Kumar, A. *History of Zawar*, Himanshu edu, Udaipur, 2017.

Kusimba, C M; Killick, D J and Creswell, R G. Indigenous and imported materials at Swahili sites on the coast of Kenya, in S T Childs (ed.) Society, Culture and Technology, MASCA 11 supplement, 1994, pp.63-77.

Lal, B B. Report on the Chemical Analysis and Examination of Metallic and Other Objects from Lothal, in S R Rao, Lothal: A Harappan Port Town (1955-62) 2 vols., ASI Memoir 78, New Delhi, (1985): 651-66.

La Niece, S, Hook, D R and Craddock, P T (eds), *Metals and Mines*; *Studies in Archaeometallurgy*, Archetype Publications, London, 2007.

Liu, H; Chen, J; Li, Y; Bao, W; Wu, X; Han, R and Sun, S. Preliminary multidisciplinary study of the Miaobeihou zinc-smelting site at Yangliusi village, in La Niece et al. (ed), 2007, pp.170-78.

Lones, T E. *Zinc and its Alloys, Pitman's Common Commodities and Industries*, London, nd.

Meyer, J J. Das altindische Buch vom Welt- und Staatsleben: Das Arthāṣāstra, des Kauṭilīya, 6 parts, Harrassowitz, Leipzig, 1925-6.

Needham, J. *Science and Civilisation in China*, V 4, Cambridge University Press, Cambridge, 1980.

Partington, J R. *A History of Chemistry*,1 pt. 1 Macmillan, London, 1961.

Penhallurick, R. *Tin in Antiquity*, The Institute of Metals, London, 1986.

Phillott, D C (ed.) *The Ā-īn-I Akbarī of Abū 'L-Faẓl* Allāmī, Vol. 1, trans. H Blochmann 1873, Asiatic Society of Bengal, Calcutta, Reprinted 1989 Low Price Publications. New Delhi, 1927.

Percy, J. *Fuels, Fireclays, Copper, Zinc and Brass*, John Murray, London, 1861.

Pinhey, A F. *History of Mewar*, reprinted 1996, Books Treasure, Jodhpur, 1909.

Pollard, M and Heron, C. *Archaeological Chemistry*, Royal Society, London, 1996.

Ponting, M J. From Damascus to Denia: the scientific analysis of three groups of Fatimid period metalwork, *Journal of the Historical Metallurgy Society* 37.2(2003):5-105

Prakash, O. *The Dutch East India Company and the Economy of Bengal* 1630-1720, Princeton University Press, Princeton, 1985.

Prakash, S and Rawat, N S. *Chemical Study of Some Indian Archaeological Antiquities*, Uttar Pradesh State Council of Scientific and Industrial Research Monograph 10, Asia Publishing House, Bombay, 1965.

Priesner, C. *Bayerisches Messing*, Franz Steiner, Stuttgart, 1997.

Rackham, H. (tr.) *Pliny: The Natural History* Vol. IX, The Loeb Classical Library, Harvard University Press, Cambridge, Ma., 1952.

Ray, P. *History of Chemistry in Ancient and Medieval India*, Indian Chemical Society, Calcutta, 1956.

Rehren, Th. Small Size, Large Scale: Roman Brass Production in Germania Inferior, *Journal of Archaeological Science,* 26.8(1999a): 1083-87.

Rehren, Th. The same ... … but different: A juxtaposition of Roman and medieval brass making in Central Europe, in S M M Young, A M Pollard, P Budd and R A Ixer (ed.), *Metals in Antiquity*, Archaeopress, BAR International Series S792, Oxford, 1999b, pp.252-57.

Riederer, J. Metallanalysen römischer Sesterzen, *Jahrbuch für Numismatik und Geldgeschichte*, 24 (1974): 73-98

Rogers, J M and Ward, R M. *Süleyman the Magnificent*, British Museum Publications, London, 1988.

Roy, M. and Subbarayappa, B.V. (tr. and ed.) Rasarṇavakalpa*,* Indian National Science Academy, New Delhi, 1976.

Ryding, K C. Islamic Alchemy According to al-Khwarizmi, *Ambix*, 41.3 (1994):121-34.

Schaeffer-Forrer, C F A; Zwicker, U and Nigge, K. Untersuchungen an metallischen Werktoffen und Schacken aus dem Berich von Ugarit, *Mikrochimica Acta* 9.6 (1982):382-405.

Schweizer, F and Bujard J. Aspect Metallurgie de quelques objets byzantins et omeyyades decouverts recemment en Jordanie, in A. Rinuy and F. Schwiezer (eds.) L'Oeuvre d'Art sous le Regard des Sciences, Musée d'art d'histoire & Editions Slatkine. Geneve, 1994, pp.191-203.

Searle, A H. *Swedenborg's Treatise on copper* (*Opera philosphopica et mineralia III*), British Non-ferrous Metals Research Association, London, 1938.

Shamasastry, R., (trans.) *The Kauṭilīya Arthaśāstra*, Government Press, Bangalore, 1915.

Singh, R N. Analyses of metal objects', Appendix V in R S Bisht (ed.) *Early Farming Communities of the Kaimur*, Publication Scheme, Jaipur, 2004, pp. 591-603.

Sisco, A G and Smith, C S. (trans. and eds*.) Bergwerk und Probierbüchlein*, American Institute of Mining and Metallurgical Engineers, New York. 1949

Sisco, A G and Smith, C S. (tr. and ed.) *Lazarus Ercker*: *Treatise on Ores and Assaying*, University of Chicago Press, Chicago, 1951.

Smith, C S and Gnudi, M T. (tr. and ed.) *The Pirotechnia of Vannoccio Biringuccio*, Basic Books, Chicago, 1942.

Smith, CS. and Hawthorne, J G. Mappae Clavicula, *Transactions of the American Philosophical Society*,64.1, Philadelphia, 1974.

Souza, G B. *The Survival of Empire: Portuguese Trade and Society in China and the South China Sea* 1630-1734, CUP, Cambridge. 1986.

Souza, G B. Ballast Goods: Chinese Maritime Trade in Zinc and Sugar in the Seventeenth and Eighteenth Centuries, in R. Ptak and D. Rothermund (ed.) *Emporia, Commodities and Entrepreneurs in Asian Maritime Trade* c. 1400 – 1750, Steiner, Stuttgart, 1991, pp. 291-315.

Stos Gale, Z A. The origin of copper based metals from the Roman period settlement of Jakuszowice in Southern Poland, *Journal of European Archaeology*, 1.2(1993):101-131.

Sun, S and Han, R. A Preliminary Study of Early Chinese Copper and Bronze Artefacts, *Acta Archaeologia Sinica,* 3 (1981): 287-301.

Thornton, C P; Lamberg-Karlovsky, C C; Liezers, M and Young, S M M. On Pins and Needles: Tracing the Evolution of Copper-base Alloying at Tepe Yahya, Iran, via ICP-MS Analysis of Common-place Items, *Journal of Archaeological Science* 29.12 (2002): 1451-60.

Thornton, C P. Of brass and bronze in prehistoric Southwest Asia, in La Niece et al. (eds.) 2007, pp. 123-34.

Tod, J. *Annals and Antiquities of Rajputana*, originally published 1829 & 1832, Smith and Elder, London, Reprinted 1978, M NPublishers, New Delhi, 1978.Tod, M. *Roman Mining in Somerset*, The Mint Press, Exeter, 2007.

Toll, C. (tr.) Al Hamdānī: *Kitābal-Gauharatain*… Die beiden Edelmetalle Gold und Silber, Studia Semetica Upsaliensia, Almqvist & Wiksell, Uppsala, 1968.

Tripathi, I D. *Rasārṇavam Rasatantram*, Chowkhambha Sanskrit Series, Varanasi, 1978.

Tye, R and Tye, M. *Jitals*, Robert Tye, South Uist, 1995.

Ullah, S and Marshall, J. Copper, bronze and lead objects, in J Marshall, *Taxila*: *An Illustrated Account of the Excavations Carried out at Taxila* 1913-1934 II, Cambridge University Press, Cambridge, 1951, pp.564-72.

Ullwer, H. Messingherstellung nach dem alten Galmeiverfahren, *Erzmetall*, 54.6 (2001): 319-36.

Ullwer, H. Das alter Galmeiverfahren und die Erreichbarren Zinkgehalte, *Erzmetall*, 61.5 (2008): 324-27.

Wang, H; Cowell, M; Cribb, J and Bowman, S. (eds.) *Metallurgical Analysis of Chinese Coins at the British Museum*, British Museum Research Publications, 152, London, 2005.

Watson, R. *Chemical Essays* IV, T. Evans, London, 1796.

Welter, J-M. The zinc content of brass: a chronological indicator?, *Techne,*18 (2003): 27-36.

Werner, O. Uber das Vorkommen von Zink und Messing im Altertum und im Mittelalter, *Erzmetall*, 23 (1970): 259-69.

Wyckoff, D. (trans. and ed.) Albert Magnus: Book of Minerals, Clarendon, Oxford, 1967

Xu, L. Traditional Zinc Smelting Technology in the Magu District of Hezhang County of Guizhou Province, in Craddock ed. 1998, 115-32.

Yih, T D and de Kreek, J. Preliminary Data on the Metallic Composition of Some S.E.-Asian Coinage as Revealed by X ray Fluorescence (XRF) Analysis, *Seaby's Numismatic Circular*, 101.1 (1993):7 9.

Zhou, Weirong. The Emergence and Development of Brass Smelting Techniques in China, *Bulletin of the Metals Museum of the Japan Institute of Metals*, 34 (2001): 87-98.

Zhou, Weirong. The origin and invention of zinc-smelting technology in China, in La Niece, et al (eds.) 2007, pp.179-87.

Zhou, Wenli; Martinón-Torres, M; Chen, J and Liu, H. Large Scale zinc production in Fengdu, Chongqing, in the Ming period, *Journal of Archaeological Science,* 39.4 (2012): 908-921.

Zhou, Wenli. *The Technology of Large-Scale Zinc Production in Chongqing in Ming and Qing China*, BAR International Series S2835, BAR Publishing, Oxford, 2016.

Zwicker, U; Greiner, H; Hofman, K H and Reithinger, M. Smelting, refining and alloying of copper and copper alloys in crucible-furnaces during prehistoric up to Roman times, in P T Craddock and M J Hughes (eds.), *Furnaces and Smelting Technology in Antiquity*, British Museum Occasional Paper,48, London, 1985, pp.103-16.

Zwicker, U. Nondestructive and other investigations of metal objects of the Archaeological Museum, Nicosia, in G C Ioannides (ed.), *Studies in Honour of Vassos Karageorghis, Society of Cypriot Studies*, Nicosia, 1992, pp.165-77.