

### Introduction

This datasheet provides a brief introduction to the manufacture of several non-ferrous metals (zinc, mercury, antimony and arsenic) that have not been covered elsewhere in this series. The metals covered in this datasheet were often rather difficult to produce and many were used rarely. Nevertheless, these metallic elements are frequently detected in copper alloys or tin-lead alloys. Their occurrence in these contexts suggests that they were inadvertently incorporated during the smelting of another metal.

### Zinc

Zinc (Zn) is a metallic element with a lead grey colour and metallic lustre. It has low melting (419.5°C) and boiling points (907°C) which provide technical challenges for its production. Zinc is moderately reactive and consequently it does not occur naturally in its metallic state. Metallic zinc is largely unknown in Britain prior to the 18th century. Zinc is, however, regularly encountered as a component of copper alloys, especially brasses (HMS Datasheet 203) from the first century AD onwards. In Britain brasses made before the 18th century rarely contain more than 30% zinc, a composition that provides a malleable attractive gold/yellow coloured metal that can be cold worked.

In the British Isles and mainland Europe there are two main zinc minerals which are of particular interest for their historical usage, Smithsonite ( $\text{ZnCO}_3$ ) and Hemimorphite ( $\text{Zn}_4\text{Si}_2\text{O}_7(\text{OH})_2 \cdot \text{H}_2\text{O}$ ). These two minerals often occur together in the upper oxidised zones of an ore body (the lower portion is usually dominated by sphalerite, a zinc sulphide). The Smithsonite and Hemimorphite are similar in colour (white, stained brown, blue or green), lustre (vitreous) and physical appearance (botryoidal, i.e. a rounded globular form), and until the mid 19th century they were usually referred to as one with the name, *calamine*. This term is no longer used to refer to these minerals except in an archaeological or historical context. Zinc deposits may form in conjunction with a variety of other ores but in Britain the strongest associations are with lead ores.

The direct smelting of zinc is difficult due to the low boiling point of the metal. Reduction of zinc oxide to zinc with charcoal requires a temperature of at least 1000°C, however, at this temperature the zinc will be a vapour. Under ordinary circumstances, therefore, the smelting of ores containing zinc would not recover significant amounts of zinc. Early brasses appear to have been made using a cementation process (see below) while the isolation of metallic zinc was achieved using a distillation process (see below).

A cementation technique for the manufacture of brass was developed in the Near East in the first millennium BC and the technique is first known in Britain in the first century AD. Cementation brass production continued until the 19th century when the production of metallic zinc by distillation made the process obsolete. The essential element of the cementation process was that the zinc ore was heated with charcoal and metallic copper in a sealed crucible. The

presence of charcoal in the crucible provided the reducing atmosphere that was necessary to reduce zinc oxide to zinc. This would be achieved at a sufficiently high temperature that the zinc would be a vapour but the fact that the crucible was sealed would ensure that the zinc did not escape. The zinc vapour would diffuse into the metallic copper in the crucible and form brass. The cementation process is described in varying degrees of detail by a number of medieval and post-medieval written sources. The later sources mention charging copper as small pieces.; this would provide the greatest surface area and so would probably ensure that zinc diffusion occurred quickly and effectively. The same sources often indicate that the cementation crucibles would be heated sufficiently to reduce the zinc and form a vapour but the resulting brass would not be melted until the zinc reduction was completed. Chemical analyses of early brasses show that before the late medieval period these had up to c28% zinc. It is likely that the nature of the cementation process was such that the production of brasses with greater proportions of zinc would be difficult.

Archaeological evidence for cementation brass production has rarely been identified in Britain and usually comprises crucibles. The prolonged exposure of these crucibles to high concentrations of zinc vapour tends to turn them a bluish-purple colour (due to the formation of zinc-aluminium spinel crystals). These sorts of crucibles have been recovered from both Roman and post-medieval sites. The scientific examination (HMS Datasheet 110) of the crucibles, as well as a range of other materials such as casting waste, will help to confirm that they are the product of brass cementation.

The manufacture of metallic zinc is likely to have been developed in India in the 12th century and by the 16th century small amounts of metallic zinc were being imported to Europe. Excavations in India have confirmed that the zinc was produced by distillation. The zinc ore was powdered and mixed with organic material which would act as a reducing agent. This was then packed into a cylindrical vessel and the opening almost completely closed up. These vessels (properly speaking retorts rather than crucibles) were inverted and placed in a furnace where they were heated. As the retorts were heated, the zinc oxide would be reduced to metal and this would drip from the bottom of the retort.

In Britain, William Champion patented a zinc distillation process in the 18th century, however, this is likely represent an appropriation of the Indian process rather than an independent invention. Champion established an integrated brassworks at Warmley (outside Bristol) where copper and zinc were smelted and brass manufactured and formed into finished goods. Although Champion held a patent for zinc distillation, he continued to make most of his brass using the cementation process. Slightly later written sources suggest that the distillation process required such large quantities of coal that the results zinc was expensive.

### Antimony

Antimony (Sb) is a metalloid/semi-metal with a grey colour, metallic lustre, a melting point of 630.6°C and a boiling point of 1587°C. Antimony and associated compounds have been utilised since prehistory, although early objects are extremely rare and are thought to represent opportunistic working of small deposits of native antimony.

The most commonly exploited antimony mineral was stibnite (Sb<sub>2</sub>S<sub>3</sub>), a lead-grey blackish coloured antimony sulphide with a metallic lustre. Stibnite is known to have been used as a cosmetic in Egypt from the 19th dynasty (1292–1190 BC) and was used widely across the antique world as a pigment. Antimony compounds were also used as an opacifier in glass from 1500BC to the 4th century AD in the Near East and across the Roman world. Stibnite was also used from the medieval period onwards in gold parting (separating gold from gold-silver alloys, see Datasheet 206). The term stibnite was unfortunately used in historical documents to refer both to the sulphide and the metal itself.

The earliest documentary sources recording the preparation of antimony date from the 16th century and involve a process called liquation. Ground stibnite would be placed in a crucible with a hole(s) in the base and a ceramic tube/funnel leading to a second, lower crucible. The top crucible would be heated to approximately 600°C, melting the stibnite whilst leaving impurities (*gangue* minerals) still solidified. Further processes, such as iron precipitation (Sb<sub>2</sub>S<sub>3</sub> + 3Fe → 3FeS + 2Sb) or an oxidising roast (Sb<sub>2</sub>S<sub>3</sub> + 3O<sub>2</sub> → 2Sb + 3SO<sub>2</sub>) could also be undertaken to produce the pure metal.

Analysis of Chalcolithic and Bronze Age copper alloy artefacts has shown some to contain a small percentage of antimony. This was probably not the result of deliberate alloying, but of smelting complex ores and the accidental reduction of antimony and its incorporation into the finished copper (along with a suite of other metals from the ore). Similar copper alloys are known in Britain during the medieval and post-medieval periods, although these also contain high proportions of lead. This alloy was widely used for the production of cast domestic cooking vessels (cauldrons, etc).

In Britain the production of antimony appears to have begun in the post-medieval period, with approximately 20 mines and processing sites known from documentary sources. The majority of mines (all of which had ceased production by the early 20th century) were located in the South West and North West of England and Southern Scotland. Processing sites were not limited by geology, often working with imported ores or crude antimony. The most successful of these (Cookson's Lead and Antimony Works based in Newcastle) helped the UK become, by 1972, the largest producer of antimony products in the world. Cookson's ceased operations in 2002 and the UK no longer processes or produces antimony.

Antimony was used in tin-based alloys (pewter) from the 18th century onwards, e.g. Britannia metal. Antimony was also used (with tin) to form type metal used to cast the type used in printing presses. It has been used (with tin and/or

lead) to make bearing alloys (such as Babbitt metal), type for printing presses, in bullets and lead shot, electric cable sheathing, and many solders.

### Arsenic

Arsenic (As) is a silver grey metalloid with a melting point of 631°C and a boiling point of 817°C. Arsenic is a frequent (if minor) component of early copper alloys. Arsenic compounds have a very long history of use, however, the metal was not isolated until the medieval period. The two most commonly used arsenic minerals were the sulphides orpiment and realgar which were used in the ancient and medieval world in paints and some medicines. Arsenic compounds have been used in a range of industries (e.g. glass manufacture) despite its toxicity.

Arsenic is often detected in copper alloys, especially prehistoric ones. The proportions are usually quite low and it is likely that the arsenic was simply present in the copper ores and was reduced along with copper (and sometimes other metals). Although these are not deliberate alloys, there does seem to have been some awareness of the differences between ordinary copper and arsenic-containing copper (e.g. colour and strength). In the 19th and 20th centuries, arsenic was deliberately added to a range of specialised copper alloys, such as brasses, to improve their corrosion resistance. Most arsenic has been produced as a bi-product of the smelting of other metals. Arsenic compounds are often found in association with tin ores and the roasting of tin ore will release arsenic which may be captured using condensers.

### Mercury

With a melting point of -38.8°C Mercury (Hg) is the only metal that is liquid at room temperature. Mercury occurs most frequently as cinnabar (HgS) which was used extensively as a pigment. The most common use of mercury was in gilding, that is the application of gold to the surface of silver or copper objects. Gold would be mixed with the mercury to form a liquid amalgam. This amalgam was applied to the surface of the object which was then heated to remove most of the mercury. This process (variously called fire gilding or amalgam gilding) was in widespread use across the Roman Empire by the 2nd century AD. Crucially for analytical purposes not all mercury is removed, and scientific analysis of any gilded objects can usually detect the element (see HMS Datasheet 106).

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