ANNEX

HISTORICAL PRODUCTION AND USES OF LEAD

HISTORICAL ACCOUNTS OF LEAD SMELTING

Primitive lead smelting hearths and furnaces, dating from ancient times, have been found in many parts of the world. The smelting of pure galena is a simple operation, and appears to have been discovered independently wherever the ore was found. (Pulsifer, 1888.)

The ancient Egyptians, Phoenicians and others in the Middle East were well acquainted with simple metallurgy, and are believed to have imparted their knowledge to the Hebrews, Greeks and Romans. There are several references to extraction metallurgy made in the Old Testament of the Bible, showing that this was known at the time (e.g. Ezekiel, 22:19-20 - dated 593 BC - "As they gather silver, and brass, and iron, and lead, and tin, into the midst of the furnace, to blow the fire upon it, to melt it . . ." - cited by Nriagu, 1983).

Many simple hearths consisted of little more than a low circular wall of stones built on a hillside, with perhaps a channel to direct the molten metal. This technology had hardly changed from ancient times until the Industrial Revolution in Europe. A German scientist, George Agricola, gives exhaustive descriptions of mining and metallurgy technology in his work (1556, De Re Metallica). A description of one type of "furnace", cited by Tylecote (1992) follows:

"They heap up two wagon loads of charcoal on some hillside which adjoins a level place, a layer of straw is placed on top and on this is laid as much pure lead ore as the heap can bear; then the charcoal is kindled and when the wind blows, it fans the fire so that the ore is smelted. In this way the lead, trickling down from the heap, falls on to the level and forms broad thin slabs."

This furnace type was also typical of British furnaces of the time. Agricola also describes some more sophisticated versions, some involving chimneys and upper chambers to collect some of the metal vapour and dust lost (Pulsifer, 1888).

The interested reader can refer to Pulsifer, 1888, Notes for a history of lead; Nriagu, 1983, Lead and Lead Poisoning in Antiquity; and Tylecote, 1992, A History of Metallurgy, for descriptions of simple furnaces and smelting techniques used by native American women, ancient Britons, native Peruvians, and other accounts of smelters in India, Iran and Japan. A more recent example of the crudest of methods is how early European settlers in Missouri learned how to smelt lead for bullets. They made a fire in the hollow of a fallen tree or old tree stump, threw in pieces of galena found on the ground, and recovered the lead from the ashes. (Pulsifer, 1888, and Nriagu, 1983 citing Schoolcraft, 1819.)

Such simple technology is possible for lead, as lead oxide can be reduced in charcoal or wood fires below 800°C, and more importantly, lead can undergo a double decomposition reaction, in which lead ore reacts with ore which has been oxidised at the top of the furnace, to yield lead metal and release sulphur dioxide gas.

This process was very simple, but had a number of problems. No more than two thirds of the lead was recovered by such primitive methods (Pulsifer, 1888), often a lot less. The remainder was lost to the slag (the material which collects over the top of the molten metal, also called "lead ashes" by early writers) and as fume. Thus it was only worthwhile exploiting ores very rich in lead, and even ores containing 20% lead would probably be discarded. (Pulsifer, 1888.)

It was observed that vegetation was damaged for a considerable distance around such furnaces, and the soil was poisoned (Tylecote, 1992), probably from the lead fume and sulphur dioxide liberated.

Old lead workings are a current source of lead in the environment. Some of these early slags have proved to be a profitable source for lead exploitation by more modern methods. Smelting is now carried out under more controlled conditions.

HISTORICAL OVERVIEW OF THE USES OF LEAD

There is evidence of lead workings and artefacts from very early periods, in excavations dating well before the time of the Roman Empire. The earliest known example of metallic lead is a metal figure recovered from the Temple of Abydus in Upper Egypt, considered to date from 4000BC; lead-rich glazes have also been found on pottery in ancient Egypt. A host of other applications are described below. However, such finds are generally small in number. Lead was less prized than the other metals - gold, silver, copper, tin and later iron - known in antiquity, as its dull lustre and softness did not make it particularly suitable for jewellery or weapons.

Prior to the time of the Roman Empire, lead extraction appears to have been principally in order to obtain silver, as the two metals frequently occur together. (Nriagu, 1983.) However, following the beginning of this era, lead was used on a large scale, as a useful material in its own right, for plumbing, tank linings, kitchenware and a host of miscellaneous uses. The use of lead declined after the collapse of the Roman Empire, but in the Middle Ages in Europe, lead began to

be used again for many applications. Some of these applications, such as for water piping and in paints, have recently been phased out, or at least greatly reduced, in view of the potential for risks to health; however, some continue to this day.

Lead piping

Lead has been used in water piping in many cultures since ancient times. Examples include pieces recovered from 4th millenium remains in Mesopotamia (Aitchison, 1960, cited in Nriagu, 1983), from Persia, dated from 1000-500BC (Partington, 1935, cited Nriagu, 1983), Egypt (Pulsifer, 1888) and ancient Greece. However, it was during the Roman Empire, with the large demand for water supplies, that the demand for lead took off. It is believed that the Romans could have learnt lead plumbing technology from the Greeks (Nriagu, 1983); their advances were in terms of implementing large scale application. The English word *plumbing*, referring to water piping, derives from the Latin word for lead, *plumbum*.

It was known since early times that lead could cause ill health (Pulsifer, 1888), and an ancient writer Vitruvius recommended that earthenware pipes be used to ensure wholesome water supply. (Pulsifer, 1888) Another writer, Pausanias referred to a particular area where the water from the hot springs destroyed the pipes within a few years - it is assumed by Pulsifer, (1888) that the water contained hydrogen sulphide, and thus was unusually corrosive. However, this did not deter the Greeks and Romans from using lead for most of their piping.

Constructional / architectural purposes

Lead used as flashings (the weathering of intersections, for example, between roof and chimney, or where a drain joins the gutter), covering of cesspools, roofing, and damp-proofing of foundations, was known in ancient times (Nriagu, 1983). Perhaps the most striking example is the huge hanging gardens of Babylon, presumed to have been built by King Nebuchadnezzar (605-562BC) for his wife: these contained lead linings separating the soil from underlying stone structure, to retain the soil's moisture. (Mothes, 1889, cited in Nriagu, 1983; Diodorus, cited in Pulsifer, 1888)

Lead was also widely used for joining masonry, by pouring molten led into the joints themselves, or around iron or bronze clamps for extra strength. (Nriagu, 1983, Pulsifer, 1888) For more ordinary applications, wire or bands of lead metal were used to provide reinforcement, for example, for large amphorae used to store water and wine. (Nriagu, 1983, Pulsifer, 1888)

As already mentioned, extensive usage of lead began with the Roman Empire, and the great desire for water, and bathing. In addition to piping, water supply required the construction of tanks, baths and the like, which were commonly lined with lead. Lead was sometimes used for other purposes, such as the roofing

of the old senate building in Constantinople, erected by Emperor Constantine, (306-336 AD).

Later, from Medieval times in Europe, lead was used in cames for stained glass windows, for roofing, piping, and other uses. Its use was not universal: lead being abundant in Britain, has traditionally been used there for roofing and even cladding of furnishings (Pulsifer, 1888); however, some other countries have traditionally favoured alternative materials, such as copper and zinc, for such purposes.

Leaded bronzes

Leaded bronze artefacts, dating from bronze age era, have been found in many areas, including Babylonia, Egypt, Greece and China and Europe. It is believed that lead was added deliberately, to lower the melting temperature and thus facilitate casting, and possibly also to harden the copper. It could also have been added as a cheap diluent in the more expensive copper (Tylecote, 1992), though in later times highly leaded bronzes were more prized (Pulsifer, 1888) It is interesting to note that leaded bronze was widely used for statues and statuettes, but weapons found at such sites contained much smaller amounts of lead. (Adding tin instead would give much better properties)

Statues, statuettes, figures

Such articles made of lead or lead alloys have been found from many ancient cultures. Artefacts from ancient Egypt date from earlier than 3000BC; small figures of soldiers from Sparta and Athens are believed to be even older (Rhousopoulos, 1909, cited in Nriagu, 1983). Effigies of sacred figures, particularly animals, were used in Assyria from 1400BC; more recently, Greek and Roman finds include a great number of figures of nude women, believed to represent Diana and other goddesses. Small figures were probably also used as children's toys. (Nriagu, 1983, Pulsifer, 1888)

Several thousand lead-based axes, found in Brittany (north west France), are dated to around 700BC (Nriagu, 1983). These would have been useless as tools or weapons; it is believed they were made for ritualistic purposes (Tylecote, 1992) or possibly as a form of currency (Nriagu, 1983).

Currency and tokens

Lead, and alloys rich in lead, have been used for millenia in the form of weights, figures, and coins. Its use was widespread in ancient Assyria, from around 2000BC, with lead animal heads being used as currency. (Nriagu, 1983)

Many finds of coins with high lead contents at sites from ancient Greece, India - the Andraha dynasty, dating from late second century BC to early third century AD, and ancient China. (Nriagu, 1983) Lead and leaded bronze coins were widely used in the Roman Empire. A large number of lead medals and tokens

were also in use, which may also have had a monetary value. (Pulsifer, 1888) The use of lead for counterfeit purposes, either by addition to bronze, or plating coins with silver or gold, has also been known since ancient times. It is referred to in texts from ancient Rome, Greece and China. (Nriagu, 1983, Pulsifer, 1888) Lead money has also been used in Europe from about the Middle Ages. It was not the preferred metal for coinage, and some lead coins would have been counterfeit, plated with silver; others were probably tokens, with presumably little monetary value. Official money was made from lead, for example, at times of war, when other metals were in short supply. (Pulsifer, 1888)

Many finds of lead tokens in Medieval France have been made. From 15th to 17th centuries, they were commonly used to denote membership of a professional guild. (Pulsifer, 1888) Others would have been used for religious purposes, or as lucky charms.

Vessels, kitchenware

Lead and pewter have been used for such purposes since very early times, in ancient Persia, Egypt, and later by the Greeks and Romans. A whole assortment of vases, kettles, tableware and cooking pots were in wide use during the Roman Empire. Pewter tableware - consisting of about 50% tin, 50% lead, was generally used by those who could not afford silver, but lead pots were actually preferred for preparation of certain dishes. The most notable were residues of boiled down fruit, which were used as cheap sweetening ingredients. Cooking in lead vessels, rather than copper, was reported by classical authors (Pliny, Cato, Palludius, cited in Nriagu, 1983) to improve the flavour (sweeten the food) and aid preservation of the dishes. Lead readily dissolves in organic acids such as those present in fruit and wine, and some such dishes would have undoubtedly been contaminated with dangerously high levels of lead.

Similarly, pewter and lead tableware was demanded by the nobility in Europe in the centuries after the Middle Ages, as silver was scarce. It was certainly in use in England by the 15th century, and in France before then. Pewter was also used to make objects of art. (Pulsifer, 1888)

The possibility of plumbism from drinking from cups made of lead, or highly leaded bronzes, or using these metals for wine storage vessels, is also discussed by Nriagu (1983). Such vessels were apparently widely used by nobility in several Chinese dynasties, for drinking fermented "wines". Bronze vessels made by European Celts generally had very high lead contents, and drinking wines from such vessels was probably not advisable. Early Christian missionaries would have usually used lead or leaded bronze cups for sacramental wine, again, potentially dissolving significant amounts of lead. Lead itself was also widely used for repairing broken pottery jars and pots, including those used for the storage of wine.

A more bizarre application of lead, and also tin and copper, was in the quality control of wine. Strips of the metals were glued to the inside of the vat lid, the vat

sealed for 40 days. If the strips were found to be clean, rather than covered with scale or bubbles, the wine was pronounced good. This practice developed into leaving metal strips permanently in wine vats, presumably highly contaminating the beverages. This was performed in Europe until well into the Middle Ages. (Nriagu, 1983)

Stationery and seals

Lead tablets used for inscriptions were used in Roman and Medieval times. They were used to provide durable written records, or to record prayers, invocations and curses. (Pulsifer, 1888) The Phoenicians used inscribed lead sheets, dropped into the tomb, as a means of sending messages to the dead. (Partington, 1935, cited in Nriagu, 1983) Lead seals have been attached to messages and merchandise since ancient times, In fact, their use on bales of cloth was required by law in England during the reign of Henry VIII. (Nriagu, 1983) Lead and lead compounds were also used as "pencils" or incorporated into inks.

Weights

Lead has been used since ancient times as standard weights, because of its high density, and inertness in air. The metal was used in almost every ancient weight class known (Nriagu, 1983), and became widely used in the Greek period, and more so during the Roman Empire. There are numerous references to the use of lead as anchors for ships. (Pulsifer, 1888) Unscrupulous use of lead to weight dice in ancient Greece was noted by Aristotle. (Pulsifer, 1888)

Burial of the dead

Lead has been used for coffins and coffin linings because it does not perish. Many examples have been found in England dating from Roman times, though few elsewhere from that period; it is thought to have been used here because lead was abundant and relatively cheap. (Pulsifer, 1888, Nriagu, 1983). The Anglo-Saxons did not bury their dead in lead, but it was sometimes used after the Middle Ages for the burial of nobility, for example for King Richard II. Some tombs included inscriptions and ornamental patterns. (Nriagu, 1983, Pulsifer, 1888)

Warfare, weapons, punishment

One of the earliest weapons of war was the sling, initially used to project stones at the enemy. Slugs or pellets of lead came in to use by Greek armies in the 5th century BC; it is reported that slingers from Rhodes could throw their missiles twice as far as the opposing Persians, who were using rocks. (Xenophon, cited by Nriagu, 1983) They were cast to shape, and often bore inscriptions such as an invocation to the gods, an insult or joke about the enemy, or message to companions. (Nriagu, 1983, Pulsifer, 1888) Other uses of lead in ancient warfare

were the pouring of molten lead from battlements on to invaders, or dropping large masses of solid lead on to them or their equipment. (Nriagu, 1983, Pulsifer, 1888) Later applications of lead in battles included cannon balls. Punishment for crimes in Greek and Roman times included lifetime of labour in the mines, with large pieces of lead strapped to the convict's body.

Glazes, enamels and glasses

A glaze is a glassy coating applied to ceramics, for reasons of decoration, or to give a gloss. Examples of pottery glazed with glazes which are rich in lead (in the chemical form lead oxide) are found in ancient Egypt, China, the Near East, and Rome. Besides being cheap, readily available, and easily fusible, such glazes have advantages of good adherence to, and compatibility with the substrate, high gloss and bright colours are possible, and the glaze lasts without devitrifying (crystals forming within the glaze, which can spoil it). However, such glazes were not universally used, and unleaded alkali glazes appear to have been more widespread. Vessels glazed with lead compounds have the potential to release lead into contents, particularly acidic wines and fruit juices, and to contribute to lead poisoning (though modern manufacturing and testing procedures limit this).

Leaded glasses, though sometimes of similar composition to glazes, apparently developed separately. Many examples of opaque, brightly coloured glass, have been found in many areas of the Middle East, dating from around the 15th century BC. Lead was added to silicate glasses in order to make melting easier, and also to add colour, opacity, or increase the brilliance of the glass.

Pigments and paints

Many compounds of lead are strongly coloured, and also durable, and this has been exploited since very early times. Red and yellow oxides of lead were used for purposes of decoration, and it is thought that early peoples attributed magical properties to them. (Nriagu, 1983) Ancient Egyptians, Assyrians and Hindus decorated their temples with bright colours, which would have included some compounds of lead. (Nriagu, 1983, Pulsifer, 1888) Galena (lead sulphide) was widely used as black eye paint in many ancient Middle Eastern cultures (Nriagu, 1983); its use continues to this day in India. (This eye paint was believed to be able to treat eye diseases.)

There are several forms of lead oxide, and the colour of oxidised lead can range through white to shades of yellow and red. These were used as cosmetics in Europe, the Middle East, India and China, and also found use with artists for painting and decoration. Red lead was less favoured, because it darkened with time.

"White lead", an intimate mixture of lead carbonate, hydroxide, and possibly oxide, makes a very durable white paint, which has been much exploited from ancient times until a few decades ago. This compound was manufactured by the

ancient Greeks, Romans and Chinese. (Nriagu, 1983.) Later, it was manufactured in many countries in Europe from the late Middle Ages, and appeared to be the preferred choice of white pigment. (Pulsifer, 1888.)

Medicinal uses of lead

Present day understanding of the effects of lead and its compounds on health, of both humans and other organisms, is that it does not have any beneficial effects whatsoever, and that excessive amounts can be very harmful. However, although the poisonous effects of lead were known even in ancient times, it was actually prescribed for medicinal purposes. Lead was used in ancient India to treat indigestion. (Pulsifer, 1888.) The Egyptians, Hippocrates and others, also considered it therapeutic, and Pliny describes several remedies which use lead: "for the removal of scars . . . and as an ingredient in plasters, for ulcers, and for the eyes etc." (Pliny, Natural History, book XXXIV chapter 1, cited Pulsifer, 1888.) Lead was generally considered to have cooling properties; even last century lead acetate was regarded as cooling, and used as a soothing lotion. Medicinal ointments were believed to work much better if kept in lead containers. (Pulsifer, 1888.) Lead also found application in dentistry, and was used in fillings in Europe up to the 17th century. (Nriagu, 1983.)

REFERENCES TO ANNEX

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- Nriagu, J.O. 1983, Lead and Lead Poisoning in Antiquity, Wiley.
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