ZINC *Protects!*

Discovering the 8th Metal

A History of Zinc

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Centuries before zinc was discovered in the metallic form, its ores were used for making brass and zinc compounds were used for healing wounds and sore eyes. Although the word brass frequently occurs in the Old Testament, there is little evidence that an alloy of zinc and copper was known in early times. The word translated "brass" might equally well be rendered bronze or copper, both of which were in common use.

In the latter part of the thirteenth century, Marco Polo described the manufacture of zinc oxide in Persia and how the Persians prepared tutia (a solution of zinc vitriol) for healing sore eyes.

The Roman writer Strabo (66 B.C. - 24 A.D.) mentioned in his writings that only the Cyprian ore contained "the cadmian stones, copper vitriol, and tutty," that is to say, the constituents from which brass can be made. It is believed that the Romans first made brass in the time of Augustus (20 B.C. to 14 A.D.) by heating a mixture of powdered calamine, charcoal and granules of copper. Roman writers observed that coins made from orichalcum were undistinguished from gold.

Figure 1: Schematic representation of the Indian method for producing zinc.

Zinc in India

The production of metallic zinc was described in the Hindu book *Rasarnava* which was written around 1200 A.D. The fourteenth century Hindu work *Rasaratnassamuchchaya* describes how the new "tin-like" metal was made by indirectly heating calamine with organic matter in a covered crucible fitted with a condenser. Zinc vapour was evolved and the vapour was air cooled in the condenser located below the refractory crucible (Figure 1). By 1374, the Hindus had recognized that zinc was a new metal, the eighth known to man at that time, and a limited amount of commercial zinc production was underway.

At Zawar, in Rajasthan, great heaps of small retorts bear testimony to extensive zinc production from the twelfth to the sixteenth centuries. The tubular retorts are about 25 cm long and 15 cm in diameter with walls about 1 cm thick. A small diameter tube was sealed onto the open end and the zinc vapours likely condensed in this. The retorts were closely spaced in a furnace which was probably heated with charcoal fanned by bellows. Both zinc metal and zinc oxide were produced. Zinc was used to make brass whereas the oxide was used medicinally. Over 130,000 tons of residue remain at Zawar and this represents the extraction of the equivalent of 1,000,000 tons of metallic zinc and zinc oxide.

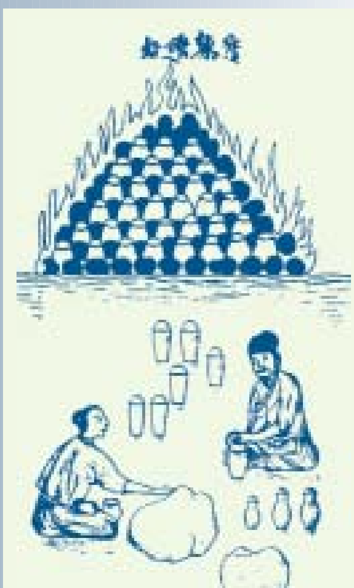

Figure 2: The Chinese learned about zinc production sometime around 1600 A.D.

Zinc in China

From India, zinc manufacture moved to China where it developed as an industry to supply the needs of brass manufacture. The Chinese apparently learned about zinc production sometime around 1600 A.D. An encyclopedia issued in the latter half of the sixteenth century makes no mention of zinc, but the book *Tien-kong-kai-ou* published early in the 17th century related a procedure for zinc manufacture. Calamine ore, mixed with powdered charcoal, was placed in clay jars and heated to evolve zinc vapour. The crucibles are piled up in a pyramid with lump coal between them (Figure 2), and, after being brought to redness, are cooled and broken. The metal is found in the center in the form of a round regulus. Zinc production expanded and metal began to be exported.

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Zinc in Europe

Figure 3: Albertus Magnus described the production of brass.

Albertus Magnus (Figure 3) (ca. 1248) described how either calamine or furnace tutty might be used to colour copper gold. He suggested that a more golden lustre might be obtained by sprinkling crushed glass on top of the mixture in the crucible to form a slag which would help prevent the escape of the zinc vapour - in other words, increase the zinc content of the brass.

Biringuccio (ca. 1540) has the next most complete description of brass making. He described how either calamine or furnace tutty could be mixed with broken up pieces of copper and sprinkled with a layer of powdered glass, then heated in a closed crucible for 24 hours.

Agricola (Figure 4) in 1546 reported that a white metal was condensed and scraped off the walls of the furnace when Rammelsberg ore was smelted in the Harz Mountains to obtain lead and silver to which he gave the name "contrefey" because it was used to imitate gold. This often consisted of metallic zinc, although he did not recognize it as such. He observed, furthermore, that a similar metal called "zincum" was being produced under similar circumstances in Silesia by the local people. Paracelsus (1493-1541) (Figure 5) was the first European to state clearly that "zincum" was a new metal and that it had properties distinct from other known metals.

Figure 4: Georgius Agricola (1490-1555) observed in 1546 that a metal called "zincum" was being produced in Silesia.

Thus, by about 1600, European scientists were aware of the existence of zinc. All the metal they had examined, however, had likely been imported from the East by Portuguese, Dutch and Arab traders. However, there was a profusion of names quite unrelated to the local names for zinc ores. These included tutenag - derived from the Persian tutiya, calamine, which became the English tutty, zinc oxide - and spelter, likely from the similar coloured lead-tin alloy, pewter, or the Dutch equivalent, spiauter or Indian tin which the British scientist Robert Boyle latinised to speltrum in 1690 from which originates spelter, the commercial term for zinc. The word tutia, an old name for zinc oxide, is derived from a Persian word that means smoke and refers to the fact that zinc oxide is evolved as white smoke when zinc ores are roasted with charcoal.

In Renaissance times, latten (or laten, laton, lattyn) became the common English word for brass, akin to the French laiton (= brass) and Italian latta (= sheet brass), and probably based on the Latin latte or lathe (= sheet). The origins of the German word for brass, Messing, may be related to the Latin massa (= lump of metal). The modern English brass may be related to the French braser (= braze or solder). The word "zinc" may be derived from the Persian word sing meaning stone. In Arabic, zinc is known as kharseen, i.e. Khar from Al-Ghar = mine, seen from Al-Seen = China, hence kharseen, the metal from Chinese mines. The spelter trade with the East flourished throughout the seventeenth and first half of the eighteenth centuries, although there seem to be no records concerning the tonnages involved.

In an extensive research "On the method of extracting zinc from its true mineral, calamine", Andreas Marggraf (Figure 6) in 1746 reduced calamine from Poland, England, Breslau and Hungary with carbon in closed retorts and obtained metallic zinc from all of them. He described his method in detail, thereby establishing the basic theory of zinc production. Marggraf also showed that the lead ores from Rammelsberg contained zinc and that zinc can be prepared from sphalerite. Marggraf was probably unaware that in 1742, the Swedish chemist Anton von Swab (1703-1768) had distilled zinc from calamine and that, two years later, he had even prepared it from blende. Since the vapors rose to the top of the alembic before passing into the receiver, this process was called distillation per ascendum. In 1752 Swab and another Swedish chemist Axel Fredrik Cronstedt (1722-1765) developed at government expense the use of Swedish zinc ores for the manufacture of brass, to avoid the necessity of importing calamine.

Figure 5: Paracelsus (1493-1541) was the first European to state clearly that "zincum" was a new metal.

The knowledge of deliberate zinc smelting in a retort was acquired by an Englishman on a visit to China just prior to 1740. A vertical retort procedure was developed by William Champion (1709-1789) and by 1743 a zinc smelter had been established at Bristol in the United Kingdom. A charge of calamine and carbon was sealed into a clay crucible having a hole in the bottom. This was luted onto an iron

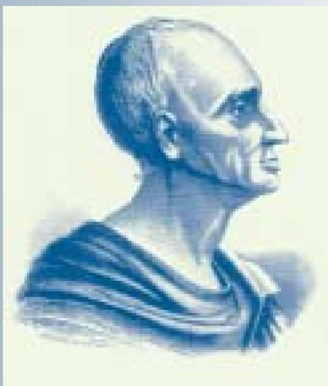

Figure 6: Andreas Marggraf (1709-1782) fully described the production of zinc from calamine.

Figure 7: William Champion's zinc smelting furnace.

tube extending below the crucible furnace into a cool chamber below. The closed end of the iron tube sat in a tub of water and it was here that the metallic zinc was collected (Figure 7). The distillation took a total of about 70 hours to yield 400 kg of metal from all 6 crucibles positioned in the furnace. An annual production rate of 200 tons has been suggested for the works at that time.

This type of apparatus continued to be employed until 1851 although it was fuel inefficient, consuming 24 tons of coal for every ton of spelter produced. In 1758, William's brother, John, patented the calcination of zinc sulfide to oxide for use in the retort process, thereby laying the foundation for the commercial zinc practice which continued well into the twentieth century. The English zinc industry was concentrated in Bristol and Swansea.

The Welsh process was a batch operation which required withdrawing the crucible and retort after each cycle. It was labour intensive and fuel inefficient. A major technological improvement came with the development of the German process by Johann Ruberg (1751-1807) who built the first zinc smelting works in Wessola in Upper Silesia in 1798 which used the horizontal retort process developed by him. The principal advantage of this technique is that the retorts were fixed horizontally into the furnace allowing them to be charged and discharged without cooling. By placing the retorts in large banks, fuel efficiency was greatly increased. The raw material initially used was zinc galmei (calamine), a by-product of lead and silver production. Later, it became possible to produce zinc directly from smithsonite, an easily smelted ore. This was shortly followed by the use of zinc blende, which had first to be converted into the oxide by roasting. After this development, other smelting works were soon erected in Silesia near the deposits, in the areas around Liège in Belgium, in Aachen, in the Rhineland and Ruhr regions in Germany.

The first Belgian plant was built by Jean-Jacques Daniel Dony (1759-1819) in 1805 and also used horizontal retorts but of slightly different design. A larger plant was built in 1810. This was the predecessor of the Societé de la Vieille Montagne which a few years later became the largest zinc producing company in the world.

Zinc production in the United States started in 1850 using the Belgium process and soon became the largest in the world. In 1907, world production was 737,500 tons of which the USA contributed 31%, Germany 28%, Belgium 21%, United Kingdom 8%, and all other countries 12%.

The excellent resistance of zinc towards atmospheric corrosion soon led to its use in sheet production. The possibility of rolling zinc at 100-150°C was discovered as early as 1805 and the first rolling mill was built in Belgium in 1812. More such mills were built in Silesia from 1821 onwards. Hot-dip galvanizing, the oldest anticorrosion process, was introduced in 1836 in France. This became possible on an industrial scale only after the development of effective processes for cleaning iron and steel surfaces. At first, only small workpieces were zinc coated. Continuous hot-dip galvanizing of semi-finished products and wire came later. In the United States, the rich ore deposits led to rapid growth in zinc production in 1840, so that by 1907, Germany, which had for long been the world's leading producer of zinc, was left behind.

Zinc was produced for about 500 years from its oxide ores which are far less abundant than the sulfides, before the sulfides became the major source of supply. The technology of zinc production changed gradually during the centuries towards a more pyrometallurgical route. However, this tendency underwent a radical change during World War I when the roasting-leaching-electrowinning process was introduced and in the 1980's, when pressure leaching-electrowinning offered another practical route to zinc production.

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