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Historical Metallurgy

Zinc — The metal from the East

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Introduction

Centuries before zinc was prepared in metallic form, its ores were used for making brass and zinc compounds which 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. 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 AD, 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 BC to 24 AD), mentioned in his writings that only Cyprian ore contained “the cadmium stones, copper vitriol, and tutu,” the constituents from which brass can be made. He also mentioned “a stone which, when burned, becomes iron, and then, when heated in a furnace with a certain earth, distills mock silver (zinc); and this, with the addition of copper, makes mountain-copper (orichalcum, or brass).” The Latin word cadmea refers both to zinc ores and to the volatilized zinc oxide obtained by roasting them. These ores included both the hydrous silicate (calamine) and the carbonate (smithsonite).

It is believed that the Romans first made brass in the time of Augustus (20 BC to 14 AD) by heating a mixture of powdered calamine, charcoal, and granules of copper, by keeping the contents of the crucible below the melting point of copper. After the zinc vapour had reacted with the copper, the temperature was raised to melt the brass. Roman writers observed that coins made from orichalcum were indistinguishable from gold. This was one of the incentives which encouraged alchemists to work on the transmutation of metals to make gold.

Zinc in India

The production of metallic zinc was described in the Hindu book Rasarnava which was written around 1200 AD. The fourteenth century Hindu work Rasaratnasamuchchaya described how the new “tin-like” metal was made by indirectly heating calamine with charcoal in a covered crucible fitted with a condenser. Zinc vapour was produced and the vapour was air-cooled in the condenser located below the refractory crucible (Fig. 1). By 1374, the Hindus had recognized that zinc was a new metal. It was the eighth known to man at that time, and a limited amount of commercial zinc production was under way. At Zawar, in Rajasthan, great heaps of small retorts and over 130 000 tons of residue bear testimony to extensive zinc production from the twelfth to sixteenth centuries. This represents the extraction of the equivalent of 1 000 000 tons of metallic zinc and zinc oxide.

Zinc in China

Zinc production moved from India 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 AD. An encyclopedia issued in the latter half of the sixteenth century makes no mention of zinc, however, the book Tien-kong-kai-ou published early in the seventeenth century included a procedure for zinc manufacture. Calamine ore, mixed with powdered charcoal, was placed in clay jars and heated to produce zinc vapour. The crucibles are piled up in a pyramid with lump coal between them (Fig. 2) and after being brought to redness, are cooled and broken. The metal is found in the centre in the form of a round regular. Zinc production expanded and the metal began to be exported.

Zinc in Europe

Albertus Magnus (Fig. 3) (ca. 1248) in the Holy Roman Empire of the German Nation described how either calamine or furnace tutt might be used to colour copper gold. In Italy, Birlinguccio (ca. 1540) described how either calamine or furnace tutt could be mixed with pieces of copper and sprinkled with a layer of powdered glass, then heated in

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a closed crucible for 24 hours. In Saxony in 1546, Agricola (Fig. 4) 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) (Fig. 5) was the first European to state clearly that "zincum" was a new metal and that it had properties distinct from other known metals.

Thus, by about 1600, European scientists were aware of the existence of zinc. All the metal they had examined was likely to have 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). In 1690, the British scientist Robert Boyle latinized the term to spelterum 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 smokes and refers to the fact that zinc oxide is evolved as white smoke when zinc ores are roasted with charcoal.

In Renaissance times, luten (or laten, laton, lattyn) became the common English word for brass, akin to the French laiton (brass) and Italian latta, 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 braiser (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.

In 1746, extensive research on the method of extracting zinc from its true mineral, calamine, Andreas Marggraf (Fig. 6) reduced calamine from Silesia, England, 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 blende or sphalerite, i.e., zinc sulphide. Marggraf was probably unaware that in 1742, 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 vapours rose to the top of the alembic before passing into the receiver, this process was called distillation per ascen- dum. 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.

Technology

Welsh Process

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 (1789-1799), and by 1743, a zinc smelter had been established at Bristol in Wales. A charge of calamine and carbon were sealed into a clay crucible with a hole in the bottom. This was luted onto an iron 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 (Fig. 7). The distillation took approximately 70 hours to yield 400 kg of metal from all six 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 as it consumed 24 tons of coal for every ton of spelter produced. In 1758, William Champion's brother, John, patented the calcination of zinc sulphide to oxide for use in the retort process, thereby laying the foundation for the commercial zinc practice which continued well into the twentieth century. At present the English zinc industry remains concentrated in Bristol and Swansea.

German Process

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 that he developed. The principal advantage of this technique was that the retorts were fixed horizontally into the furnace allowing them to be charged and discharged without cooling. The condensers were luted onto the open ends which simplified the task of metal recovery. 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 followed by the use of zinc oxide obtained by roasting zinc blende. 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 in the Ruhr regions in Germany.

Belgian Process

The first Belgian plant was built by Jean-Jacques Daniel Dony (1759-1819) (Fig. 8) in 1805 who also used horizontal retorts but of slightly different design (Figs. 9 and 10). A larger plant was built in 1810. This was the predecessor of the Société de la Vieille Montagne which, a few years later, made Belgium the largest zinc producing country in the world.

American Processes

Zinc production in the United States started in 1850 using the Belgian process and soon became the largest producer in the world. In 1907, the world production was 737,500 tons of which the United States contributed 31%, Germany 28%, Belgium 21%, United Kingdom 8%, and all other countries 12%. Although major improvements in retort and furnace design were made, the horizontal retort process remained, in principle, unchanged for a century and a half. Research to improve the process led to two new processes:

1. Vertical retorts process — This process was developed in 1929 by New Jersey Zinc in Palmitont, Pennsylvania. The main feature of the process is the large vertical rectangular retorts that are operated continuously. The retorts are 7.5 m high, 2.1 m long, and 0.3 m wide. They are made of silicon carbide bricks which have good thermal conductivity. Each retort is heated externally in a separate furnace. The charge to retorts is in the form of briquets composed of ZnO and coal in the ratio 1:1. Zinc vapours are collected from the top of the retorts to a condenser where they are cooled by molten zinc at about 420°C. A part of the condensed zinc is recovered as product while the rest is recycled at the condenser. The spent briquets are continuously discharged from the retort by a screw conveyor at the bottom. Each retort is capable of producing 6 tons per day zinc. Gases containing CO are burned to supply heat for the retort furnace. The normal life of a retort is three to five years.

2. Electric furnace processes — Two commercial processes were used for the reduction of ZnO using electrical energy for supplying the necessary heat of reaction. In both processes, the charge, composed of ZnO and coke, is first preheated to 850°C to 900°C in a rotary kiln fired by CO leaving the electric furnace. The difference between the two processes is in furnace design.

In the St. Joseph Lead Company process, the charge itself serves as the electrical resistance which develops the heat in a vertical furnace 1.5 m to 3.6 m in diameter and about 12 m high. Carbon electrodes are inserted through the furnace wall near the top and bottom (Fig. 11). The furnace is operated under a vacuum to accelerate the removal of zinc vapours from the top. Condensation of zinc is achieved in a bath of molten zinc held in a cooled vessel.

In the Sterling process, a horizontal arc furnace is used. The charge is introduced through the roof along the side and end walls. The electrodes come down through the roof, and the arc is struck just above the slag layer. Zinc vapours leave the furnace and are cooled in a condenser, while the oxides or iron, lead, and copper are also reduced and collected as a molten alloy below the slag layer.

Blast Furnace Process

This process was developed by the Imperial Smelting Corporation in Wales in 1957. The charge, composed of ZnO and coke, enters the blast furnace through a double bell system to avoid the escape of gases (Fig. 12). The process has the following characteristics.

Zinc oxide sinter is charged while hot, and coke, must be preheated to 800°C so that the gases leaving the top of the furnace could be maintained at about 1000°C. This high temperature is necessary to prevent the condensation of zinc in the furnace. The gases contain about 5% Zn, 10% CO₂, 20% CO, and the balance, N.

The gases enter the condenser where a shower of molten lead, at 440°C, cools them rapidly. The lead shower is created by impellers rapidly rotating in a pool of molten lead. Molten lead not only cools the gases but also dissolves the condensed zinc and thus prevents the formation of ZnO. The use of molten lead is therefore more advantageous than molten zinc although the cooling temperature is higher. The molten lead-zinc alloy then leaves the condenser at 370°C. It is allowed to cool to 440°C where
molten zinc, containing about 1% Pb, separates at the top, while molten lead, saturated with zinc, leaves at the bottom and is pumped back to the condenser. A large amount of lead is circulated due to the high temperature of the gases to be cooled as well as the latent heat liberated during the condensation of zinc which is 419 cal/g. About 400 tons of lead are circulated for every ton of condensed zinc. Thus, a plant producing 200 tons per day of zinc will have about 80 000 tons of lead in circulation in the cooling system. Lead entering the condenser contains 2.02% Zn. When leaving it, the lead contains 2.26% Zn. The alloying of lead with zinc is an endothermic process. Since the exit gases contain appreciable amounts of CO, they are first scrubbed to remove dust, then they are utilized as a fuel in the plant for coke and air pre-heating. Lead values in the ore accumu-
late as a lead bullion at the bottom of the furnace, while cadmium is volatilized together with zinc. Zinc produced by this process contains 1% to 1.5% Pb, 0.07% Cd, and 0.05% Fe. It is purified by vacuum distillation.

Hydrometallurgical Processes

A hydrometallurgical-electrowinning process was introduced during World War I by the joint effort of metallurgists from the Anaconda Company in Montana and Cominco in British Columbia to exploit the low-grade zinc concentrates which were not economical to treat by the retort process. The ZnO produced by roasting was leached by recycled acid obtained from the subsequent electrowinning step (Fig. 13). The process required extensive solution purification and was generally successful, because it yielded high-purity zinc directly but suffered from the following:

- Sulphuric acid must be produced from the SO₂ generated in the roasting step.
- A large portion of zinc was in the residue in the form of ferrite, ZnFe₂O₄, which was insoluble in the recycled acid and had to be treated in a separate circuit. Processes were developed to treat this material such as the Jarosite process but these created other problems, e.g., the final residue was more voluminous than the original, thus creating a stockpiling problem.

A pressure leaching process was developed by Sherritt Gordon (now Dynatec) in Canada in the 1970s. At present, there are four operating plants using this technology. It is based on the aqueous oxidation of zinc sulphide concentrates in dilute H₂SO₄ at 150°C and
under oxygen pressure of 700 kPa (Fig. 14). Autoclaves lined with acid-resisting bricks are used (Fig. 15). The reaction is exothermic and yields elemental sulphur which can be used to make sulphuric acid when desired. No ferries are formed, and therefore the residue can be disposed of directly and the solution can be purified in the usual way and electrolyzed to yield pure metallic zinc and acid for recycling to the leaching step.

**Applications and Environmental Problems**

The good resistance of zinc toward atmospheric corrosion soon led to its use in sheet steel production. The possibility of rolling zinc at 100°C to 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 onward. Hot-dip galvanizing, the oldest anti-corrosion 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. By 1907, Germany, which had been the world's leading producer of zinc, was left behind.

In the 1970s, the Scandinavian countries were alerted to the presence of traces of mercury in zinc sulphide ores and its contamination of the sulphuric acid produced from the SO₂ generated during the roasting of the concentrates. Such acid is usually used to make fertilizers and hence there was the possibility that mercury may enter in the food chain. Processes were immediately developed to capture this mercury and at present, nearly all zinc sulphide roasting plants worldwide have added units to remove the mercury.

**Summary**

Zinc was used with copper by the Romans in the form of an alloy known as brass, but the recognition that a peculiar metal is fixed by copper when certain earths are smelted with that metal was due to the eighteenth century chemists.

Metallic zinc was first produced in India around 1200 AD. From there, its production moved to China. It was only around 1740 that Europeans started to produce the metal becoming the eighth metal known. Because it forms as a vapour during the thermal reduction of its oxide, means have to be provided to condense the vapour rapidly to avoid its oxidation. Its method of production is difficult.

Metallic zinc was produced for about 500 years from its oxide ores, which are far less abundant than the sulphides, before the sulphides became the major source of supply of the oxide by roasting.

The technology of zinc production changed gradually over the centuries toward a more efficient pyrometallurgical route. However, this tendency underwent a radical change during World War I when the roasting-leaching-electrowinning process was introduced (Fig. 16) and finally, in the 1980s, when the pressure leaching-electrowinning came to solve the standing problems of previous technologies.

**Suggested Readings**


