

Bericht *Report*

History of Zinc, its Production and Usage

Dr. Marinanne Schönnenbeck/Frank Neumann

Introduction

Long before the discovery of zinc as a metal, zinc ore was already being used to produce the copper-zinc alloy brass as well as zinc salts for medical purposes. Objects made of brass are known from Babylonia and Assyria from 3000 BC, and from Palestine dating from 1400 - 1000 BC.

The addition of zinc to copper for the first time was proven by a piece of jewellery from around 500 BC found on Rhodos. And even if zinc was used from that date to produce brass for example, many centuries nevertheless passed until it could be identified as a metal. The name "zinc" only came into general use in the 17th century following rediscovery of the material.

As zinc only ever occurs in Nature in the form of compounds, it was initially produced from carbonate of zinc, a zinc salt. Zinc was found to be especially suitable for alloys with other metals and was therefore first of all employed to make coins. Although zinc ores have been in use since the Bronze Age, it was not until very much later that zinc was discovered to be an element, i.e. a substance that cannot be broken down further. Zinc was generally imported from India until the end of the 18th century and was considered to be very costly.

Early production and usage in India and China

Metallic zinc was produced in India around 1200 AD, and the process is described as the production of a new metal similar to tin. It involved heating the zinc ore indirectly with charcoal in a covered crucible. This produced zinc vapour, which was cooled by the ambient air in a condensation recipient underneath the crucible. This is how metallic zinc was formed (**Fehler! Verweisquelle konnte nicht gefunden werden.**).

It was Marco Polo (1254-1324) from Venice who reported the production of zinc oxide in Persia. At this time the Persians used a solution of zinc vitriol ($\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$) to treat eye inflammations. Zinc sulphate (ZnSO_4) is used in medicine as an adstringent and antiseptic even today.

By 1374 zinc had been recognised by the Hindus as a new metal, the eighth known in that day and age, and zinc production and trading was already underway on a limited scale.

Bericht *Report*

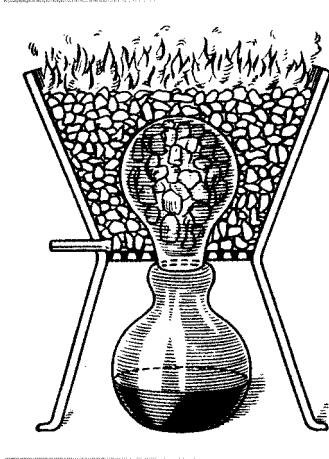


Fig. 1:

In India around 1200 AD metallic zinc was produced in a covered crucible. From there it passed into a condensation recipient, where it was cooled by the ambient air. (according to Habashi)

We also know of a modified process used in the province of Rajasthan in the northwest of India during the period between the 12th and 16th century. There tube-shaped crucibles 25 cm in length and 15 cm in diameter were equipped with a tube of a smaller diameter. The crucibles were stacked in an oven, which was heated with charcoal with the help of bellows. The zinc vapour then condensed in the tubes. This method provided for the extraction of around 1 million tons of metallic zinc and zinc oxide – as indicated by the residues found at this site. Metallic zinc was used to produce brass, while the zinc oxide was destined for medical applications.

A production process is described in 17th century China (**Fehler! Verweisquelle konnte nicht gefunden werden.**), involving mixing zinc ore in individual crucibles with powdered charcoal. They were then stacked up into a pyramid shape with coals between the spaces. This entire structure was heated until red-hot, and then cooled down and broken apart. Zinc would be found in the middle as round lumps of metal. During the Ming dynasty (1368-1644) China was already using coins containing 99% zinc and 1% silver. The production of zinc increased, and it was exported from India and China as far away as Europe.

Bericht *Report*

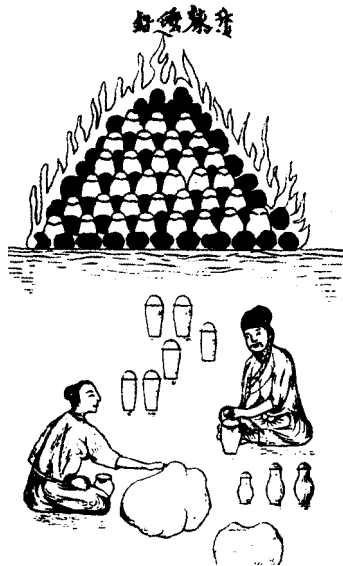


Fig. 2:

Production of zinc in 17th century China, using crucibles stacked into pyramids with charcoal between the spaces. After being heated until it was red-hot and subsequent cooling, the slag was broken apart to find the zinc in the middle. (according to Habashi)

Early production and usage in Europe

The Greek geographer and historian Strabo (64 BC to 23 AD) comments that only "Cyprian ore" contained the necessary constituents for the production of brass. He also mentions a mineral that turns into iron when burnt and, if then melted in an oven with certain constituents, "mock silver" (i.e. zinc) could be distilled. This material could itself be used to obtain brass by alloying it with copper.

It is assumed that in Rome at the time of Augustus (63 BC to 14 AD) brass was produced by heating up a mixture of powdered calamine, charcoal and granules of copper while ensuring that the temperature remained below the melting point of copper. Once the resulting zinc vapour had reacted with the copper, the temperature was increased, so smelting brass. The similarity between brass and gold probably also spurred on numerous alchemists to try to produce gold from other metals.

In the middle of the 13th century the natural scientist, philosopher and theologian Albertus Magnus (1200-1280) describes – without even knowing of zinc as a metal – a process that allowed the level of zinc in brass to be increased during smelting. This consisted of scattering crushed glass over the molten mass to make slag. This prevented the zinc escaping from this mass as vapour, so increasing the zinc content of the brass.

The works "De natura fossilium" (1546) and "De re metallica" (published in 1556) were written by Georgius Agricola (1494-1555), the humanist, physician and mineralogist from Saxony. He describes how, during the extraction of silver and lead in Germany's Harz Mountains, a white metal was deposited on the walls of the furnace and was used as an imitation for gold. The physician and natural scientist Philippus Theophrastus Paracelsus (1493-1543) was the first to clearly identify "zincum" (zinc) as a new metal, which differed

Bericht *Report*

from the other metals known at the time in terms of its properties. During this period zinc was still mainly imported from the Orient.

The word "zinc" possibly comes from the Persian "sing", which means "stone". On the other hand, it might also derive from the German term "Zincken", which was a reference to the jagged shape of calamine ore.

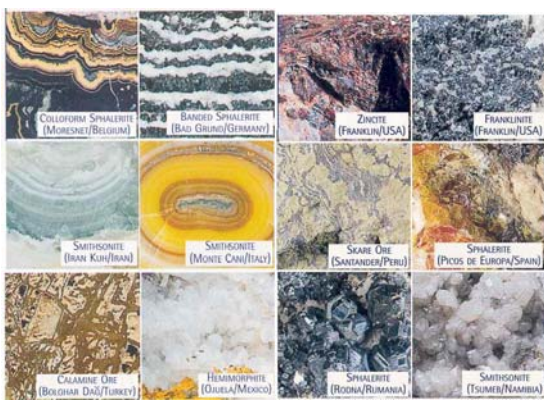


Fig. 3:
Zinc minerals (from IZA: Pocket Guide).

One major difficulty during the extraction of zinc at the time was its tendency to already vaporise below the smelting temperature, which is over 1,000 °C. With the ingress of air the zinc then combusts into zinc oxide. During smelting the resulting zinc vapour thus had to be captured and condensed without the ingress of air to ensure the deposit of metallic zinc.

In 1746 the Berlin chemist Andreas Sigismund Marggraf (1709-1782) succeeded in isolating zinc as a pure metal. In his experiment Marggraf heated zinc ores from various sources together with charcoal in covered crucibles and obtained metallic zinc from all of them. Here he demonstrated not only that the lead ores from Rammelsberg in the Harz likewise contained zinc, but also that zinc can be extracted from sphalerite.

Shortly before this date the Swedish scientist Anton von Swab (1703-1768) succeeded in distilling zinc. As the vapours ascended upwards during this process before passing into the recipient, it was known as distillation "per ascendum".

In the 18th century the metal was extracted on an increased scale in England, Upper Silesia and in the Aachen-Liège region.

The process of smelting zinc in a retort oven was observed in China by an Englishman, William Champion (1709-1789). He then developed a process using a vertical retort oven (**Fehler! Verweisquelle konnte nicht gefunden werden.**). This involved placing zinc ore with coal in covered crucibles with an opening at the bottom. The melted zinc then ran into an iron pipe extending into a cooling chamber underneath. The metallic zinc was

Bericht *Report*

collected at the closed end of the pipe, which was cooled with water. This allowed some 400 kg of metallic zinc to be extracted in an oven with 6 crucibles in a period of 70 or so hours. The first zinc smelting plant was opened by William Champion at Bristol, England in 1743.

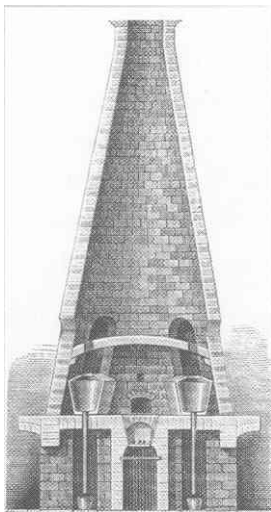


Fig. 4:

Zinc smelting oven, as used by William Champion at his zinc smelting works in Bristol. (according to Habashi)

In 1798 Johann Ruhberg (1751-1807) built the first zinc smelters in Upper Silesia using the horizontal retort oven he had developed. Here the individual crucibles were positioned horizontally in the furnace, allowing them to be charged and removed without cooling. Arranging the crucibles in banks resulted in a major fuel saving. Initially the raw material used in the process was zinc galmei (calamine), a by-product of lead and silver mining. This was followed by the use of smithsonite (ZnCO_3), an ore that is easy to smelt, and even later by zinc blende (ZnS), which was first converted into zinc oxide by roasting. This soon gave rise to new zinc works in Silesia, the Aachen-Liège region and Germany's Ruhrgebiet. Zinc blende was also produced as waste when mining for silver minerals, and its usage again became of interest later on with the emergence of new zinc extraction processes.

When the zinc blende (ZnS) was roasted, this resulted in the release of sulphur dioxide, causing major pollution of the environment around the smelting works. Only later did it become possible to convert the roasting gases almost entirely into sulphuric acid.

Bericht *Report*

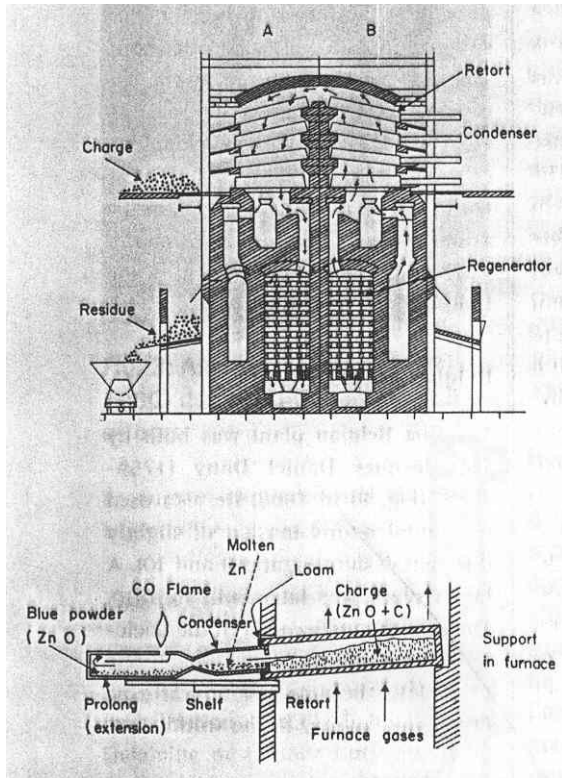


Fig. 5:

Diagram of horizontal retort oven (according to Habashi)

1810 saw the construction of a Belgian zinc works that then gave rise to the Société de la Vieille Montagne. A few years later it had already become the world's biggest producer of zinc. Here the company used a slightly modified version of the horizontal process (**Fehler! Verweisquelle konnte nicht gefunden werden.**). The zinc smelting plants in the United States also used the same method from the middle of the 19th century and by the beginning of the 20th century, they accounted for almost a third of the world production of zinc.

Once a process was developed in 1805 to roll zinc into smooth sheets of metal at between 100 and 150 °C, the material could also be used successfully in the building industry to make roof coverings, gutters and downpipes. This paved the way for the opening of the first zinc plants in Belgium and Silesia. Here zinc was mined, smelted and rolled into sheets with standard dimensions of 1 x 2 m. In the early 19th century the shining blue-white material was used by people such as Karl Friedrich Schinkel for ornamental sheet-metal work. This is recorded by a large number of technical publications dealing above all with the techniques for installing smooth sheets as well as the details of joining and connection this material. It was only in the middle of the 1960s that this so-called pack rolling process was superseded by more modern technology due to material properties now deemed to be inadequate.

Bericht *Report*



*Fig. 6:
Production of sheets of zinc using the pack
rolling process*



*Fig. 7:
Ornamental sheet-metal work at Schloss
Glienicke, built by Karl Friedrich Schinkel
between 1825 and 1828.*

The galvanisation of steel sheeting and large structural steel components then became a key application for zinc thanks to its anti-corrosion properties. From the 19th century the production of zinc rose thus together with the increasing use of steel. Zinc is also used to produce alloys (brass, red bronze, nickel silver). Another application is die-cast parts. As already mentioned, zinc is also added to drugs, cosmetics and to animal feed as a supplement.

Modern production processes

In Nature zinc is found in the form of compounds involving oxygen or sulphur. The most important zinc mineral is zinc blende (ZnS). It often occurs together with galena, iron pyrite, copper pyrite and other minerals.

The weathering of zinc blende gives rise to carbonatic and siliceous zinc minerals, known as oxidic zinc ore or calamine. In addition, zinc deposits generally contain other valuable metals on a scale that is of economic interest, with lead occurring most frequently. Other important metals are copper, silver, iron, manganese and cadmium, as well as low levels of other metals. Some 90% of zinc ore is mined by underground working. Normally the ore is processed into concentrates near the deposit site in several stages via flotation and then used as the base material for subsequent smelting.

Bericht *Report*

The following processes are available for the production of zinc from these concentrates:

- zinc electrolysis,
- the Imperial smelting process and New Jersey zinc distillation (for refining crude zinc)

There are also plants for resmelting and liquation, i.e. for thermic separation, of zinc scrap.

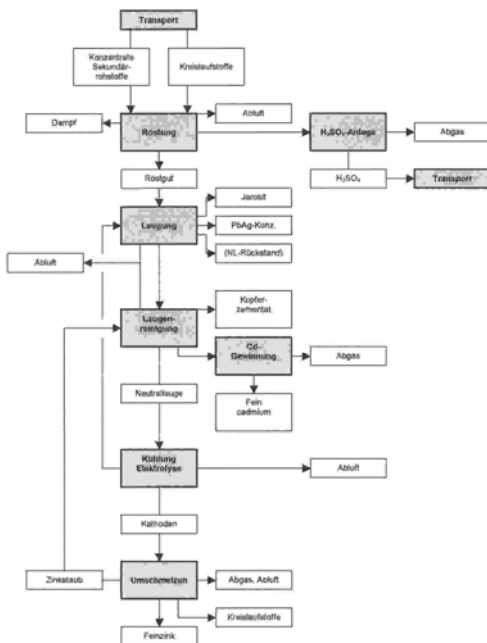


Fig. 8:

With zinc electrolysis zinc is deposited from the neutral leach on the cathode. (according to Hullmann (Publ.): Natürlich oxidierende Metalloberflächen)

High-grade zinc is produced during zinc electrolysis using a hydrometallurgical process, which involves the following steps:

- Roasting - the roasted blende is oxidised from the concentrates, producing SO₂-containing off-gas, which undergoes further processing into H₂SO₄ in a separate system,
- Leaching - the roasted material (roasted blende) is dissolved in sulphuric acid,
- Purification of leach - here accompanying elements such as copper and cadmium are separated from the leach, resulting in the so-called neutral leach,
- Electrolysis - the zinc is deposited electrolytically from the neutral leach on the cathode,

Bericht *Report*

- Resmelting - in a final step the cathodes are resmelted into blocks of zinc.

Zinc electrolysis results in a high utilisation level of the concentrates. Increasing use is also being made of secondary raw materials rich in zinc in this hydrometallurgical process for the extraction of zinc.

As a pyrometallurgical technique the Imperial Smelting process provides for the direct processing of concentrates and secondary raw materials. The main energy source is coke. In addition to the primary products of zinc and lead the process also produces slag, which can be used in the construction sector. This process accounts for some 15% of the world's zinc production.

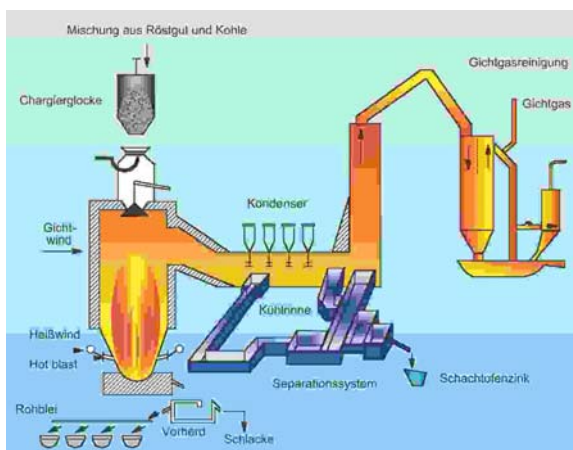


Fig. 9

Diagram showing the extraction of zinc and lead using the Imperial Smelting process in a shaft furnace (graphic Initiative Zink)

The individual steps of the IS process are as follows (**Fehler! Verweisquelle konnte nicht gefunden werden.**):

- Briquetting: secondary raw materials and "waelz" oxide are hot-briquetted,
- Roasting: concentrates are desulphurised (roasted) via sinter roasting and agglomerated with recycling materials,
- Reduction and condensation: hot briquets and sinter are reduced with coke in the IS furnace. Zinc is discharged with the blast furnace gas and condensed as crude zinc. Lead is discharged at the lower end of the furnace.

To extract high-grade zinc this is followed by two-stage distillation according to the New Jersey process, involving removal of the remaining accompanying metals and the production of high-grade zinc of great purity.

Bericht *Report*

- Liquation: the constituents of the molten metal are separated according to their different melting points; this process also produces hard zinc, an iron-zinc alloy.
- Casting: the zinc alloys and zinc are then cast.

The Waelz tube process is used when processing feedstock with a low zinc content, e.g. as occurring during recycling in particular. Here the feedstock is first formed into moist balls (pelletised) and then heated in a rotary furnace (Waelz tube). The zinc contained in the material vaporises, is oxidised and can be recovered as "waelz" oxide after cooling in a filter.

One important source of feedstock with low zinc levels is the filter dust containing zinc produced when recycling galvanised steel parts. Recycling the zinc found in such dust using the above process has represented state-of-the-art technology for many years.

Production of sheets and strips

One major advance in the production of zinc strips in predefined thicknesses was the introduction of the continuous wide-strip casting and rolling process at RHEINZINK. Here an alloy of zinc, copper and titanium is smelted in a coreless induction furnace at a temperature of approx. 760 °C. This produces master alloy blocks that are then melted in a core-type induction furnace and mixed with high-grade zinc.

The resulting alloy is next passed to the casting machine in liquid form. Here it is cooled below melting point by a closed water circulation system to produce a solid billet. This process must take place at the same speed as the following steps – rolling and winding. The billet passes through a cooling section and loop towers to compensate for any minor differences in speed to then arrive at the roll stands. Here the thickness of the material is reduced in steps. The careful coordination of pressure and cooling is used to influence the metallurgical properties of the material such as ductility, tensile strength and long-time rupture strength.

After rolling the finished strip is wound into large coils. The rolling process subjects thin sheets to stresses which are undesirable during subsequent usage. To eliminate such stresses the material is stretched, bent several times and straightened in another process. It can then be divided longitudinally and crosswise and processed for example into sheets for roofs, facades or roof drainage products.

Bericht *Report*

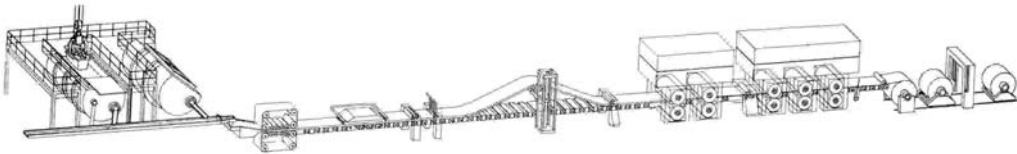


Fig. 12: In the casting rolling-process at RHEINZINK zinc strips are produced from liquid metal in the form of a coil using a continuous process

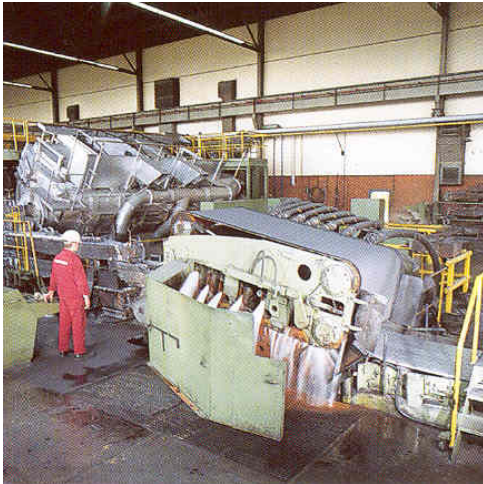


Fig. 13: In the casting machine the finished alloy is provided with the input cross-section necessary for the rolling process with simultaneous cooling.



Fig. 14: At the end of the rolling train the finished strip is wound into large coils and stored temporarily for cooling.

Bericht *Report*

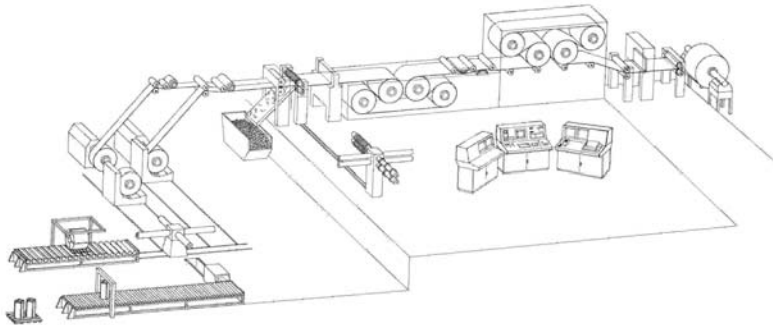


Fig. 15:

A stretching, bending and straightening system is used to eliminate stresses in the strip, which is then divided longitudinally and crosswise depending on further processing.

Deposits and reserves

The deposits of zinc ore in existence are only known as far as they have been investigated for mining in the near future. Other deposits are explored regularly, so changing the limits of availability, also depending on the technology used and the achievable price.

The zinc content of the reserves of ore definitely and probably considered to exist in 1999 was approx. 200 million t. Around half has been identified in Australia, China, the USA and Canada. The total reserves of zinc identified in terms of the metal content of the deposits are put at approx. 1.9 billion t in total throughout the world. The exploration of other resources in association with appropriate market price adjustments will ensure zinc is available on a long-term basis. In addition, some 30% of the zinc used in the world today is recovered by recycling materials containing zinc. This share is already exceeded in Germany at present and is also set to rise worldwide in coming years.

Applications and recycling today

Zinc is mainly used for the following applications:

- in the form of sheets and other semi-finished products, in particular in the building industry,
- in alloys, mostly combined with copper as brass and with aluminium to make die-cast parts – around one third of total zinc production,
- to protect steel parts from corrosion – around half of total zinc production,
- in the chemical industry as zinc oxide and zinc dust.

Zinc sheets are used in construction, not only to protect steel parts from corrosion, but also for roofs, facades and roof drainage. At the end of their service life they can be

Bericht *Report*

melted down again and reused as secondary zinc in alloys, for galvanisation or in the chemical industry.



Fig. 16:

Zinc roofs are a good solution for historical buildings even with challenging geometries.



Fig. 17:

Facade design featuring zinc with a durable, naturally patinating surface

Die-cast parts made of zinc are used for example in domestic appliances and vehicles and are shredded up with them at the end of their life. The zinc is then separated from the other materials and reprocessed.

Scrap brass contains a high level of copper and is mainly recycled directly in the brass and copper industry. Depending on the process used, the zinc either remains in the remelted alloy or is separated as zinc oxide via flue dust and forms part of new products made of zinc.

Scrap from galvanised steel parts is recycled in steel production. The zinc vaporises and is recovered as filter dust. It can then be reused for the production of zinc.

Bericht *Report*

scrap is submitted for processing and recycling via established channels. These metals can also be recycled an infinite number of times.

Zinc is an essential trace element for living organisms. The amount of zinc needed by humans depends on age, sex, possible pregnancy and nutritional conditions. The intake of zinc is regulated by an endogenic mechanism according to the requirement for and level of zinc in the diet. The intake of zinc from diet thus varies between 10-80%. The availability for living organisms may be affected by changes in the gastrointestinal tract, other substances involved and the types of food consumed. Zinc levels for an adult are around 1.5 to 3 g with a body weight of 70 kg. The elementary biological significance of zinc is underlined by the fact that it is present in every organ and all bodily fluids.

Bibliography

Habashi, Fathi:
Discovering the 8th Metal – A History of Zinc
Brussels: International Zinc Association (IZA), w/o. vol.

Habashi, Fathi:
Zinc, the metal from the east
In: Metall, 56th vol., 06/2002

Hullmann, Heinz (Publ.)
Natürlich oxidierende Metalloberflächen
Umweltauswirkungen beim Einsatz von Kupfer und Zink in Gebäudehüllen
Stuttgart: IRB Verlag, 2003

International Zinc Association-Europe (Publ.):
Pocket Guide to World Zinc
Brussels: International Zinc Association IZA, 2000

Rheinzink (Publ.):
RHEINZINK® - Anwendung in der Architektur
Datteln: Rheinzink, 2nd updated ed., repr. 2001

v. Klass, Gerd:
Stolberger Zink - Die Geschichte eines Metalls
Aachen: Stolberger Zink AG, 1956

Wellmer, Friedrich-Wilhelm:
Gewinnung und Nutzung von Rohstoffen im Spannungsfeld zwischen Ökonomie und Ökologie
In: Geowissenschaften 14 (1996), issue 2