

Review

Evaluation and Current State of Primary and Secondary Zinc Production—A Review

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Abstract: This article presents the history of zinc, its production and demand. The quantity of zinc production, both primary zinc from ores and concentrates, and secondary zinc from scrap and zinc-rich waste, was discussed. A comprehensive economic analysis covers zinc prices in the years 1960–2021. The basic methods of obtaining zinc from ores, including pyrometallurgical (Imperial Smelting Process ISP, Kivcet, Ausmelt) and hydrometallurgical (roasting–leaching–electrowinning RLE, atmospheric direct leaching ADL, Engitec Zinc Extraction EZINEX, zinc pressure leach) and their short characteristics, are presented. The global zinc market and the main areas of its application were analyzed. Technologies used for the recovery of zinc from scrap are discussed along with their characteristics. Galvanized steel is the main source of secondary zinc, both in the galvanizing process and in the remelting of galvanized steel. It can be easily recycled with other scrap steel in the electric arc furnace (EAF) for steel production. Currently, with high volatility in the price of zinc, as well as its natural resources in the earth's crust, recycling is an important activity, despite the fact that zinc concentrates have a relatively constant chemical composition, while the resulting zinc waste contains zinc in varying amounts.

Keywords: zinc; zinc production; primary zinc; secondary zinc; hot dip galvanizing process; zinc recycling



Citation: Kania, H.; Saternus, M. Evaluation and Current State of Primary and Secondary Zinc Production—A Review. *Appl. Sci.* **2023**, *13*, 2003. <https://doi.org/10.3390/app13032003>

Academic Editor: Cem Selcuk

Received: 27 December 2022

Revised: 22 January 2023

Accepted: 30 January 2023

Published: 3 February 2023



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1. Introduction

Zinc is one of the most important non-ferrous metals used in society. Its properties that protect steel against corrosion give immense economic and environmental effects [1]. However, the increasing demand for this metal may limit its availability [2,3], as zinc has been used since ancient times. Romans produced significant amounts of brass products, i.e., an alloy of copper and zinc, around 200 BC. However, the ancient Greeks knew this metal under the name “pseudargyras”, which can be translated as “fake silver”. Archaeological discoveries confirm its presence from around 300 BC in the form of artifacts made of zinc, including a sheet of zinc from Athens [4]. However, a rational and efficient method of producing zinc was not known at that time, which significantly limited its use.

Zinc was probably first obtained in India. Already in ancient Indian writings, the first descriptions of the processes of producing metallic zinc from ores were found [5]. In 1374 it was identified as a new metal. Wastes from the zinc smelter in Zawar, Rajasthan (India) testify to the large scale of zinc production in the period from 1100 to 1500 [6]. Sources report that during this period, this smelter could produce from 60,000 tons of metallic zinc [7] to about a million tons of metallic zinc and zinc oxide [8]. At the end of the thirteenth century, Marco Polo described the production of zinc oxide in Persia, where it was used in the form of pills to treat eye infections [5]. These pills, made of hydrozincite and smithsonite, were found aboard the Roman ship Relitto del Pozzino, which was shipwrecked in 140 BC [9]. At the same time, zinc production also developed in China [10]. In Europe first descriptions of experiments with calamine and the resulting product can be found in the works of Albertus Magnus (ca. 1248), Biringuccio (ca. 1540), Agricola (1546), Paracelsus

(1540) and Andreas Libavius (1596) [11–13]. In 1742 work on the distillation of zinc from calamine was carried out by the Swedish chemist Anton von Swab [13]. William Champion developed zinc production in vertical retorts and patented it. In 1743, the first zinc smelter with an annual capacity of about 200 tons was built in Bristol [14]. Oddly enough, the official discovery of zinc as a metal dates back three years later and is attributed to the German chemist Andreas Marggraf, who described the zinc production process in great detail [6]. The improved retort process was used by Johann Ruberg, who, in 1798, built a zinc smelter in Wesola in Upper Silesia [14]. The main advantage of this technique was that the retorts were mounted horizontally in the furnace, which allowed them to be loaded and unloaded without cooling. The Ruberg method became a rational and economical method for large-scale zinc production in Europe. Further zinc smelters were established in Upper Silesia, but zinc production also developed in the Liège region in Belgium, in Aachen, in the Rhineland and in the Ruhr area in Germany [6,12]. Zinc production in the United States began in 1850 with the retort process, but progress was made in the 1920s with the patenting of the continuous retort process. In 1917, a process for the electrowinning of zinc was developed (roasting–leaching–electrowinning). Another modification of the zinc production process was the introduction of pressure leaching in the 1980s [13].

The presented description of zinc production in the old days indicates problems with its acquisition. With the development of civilization, there was a leap in the industry's interest in zinc, which entailed the need to develop rational and efficient methods of obtaining it, which consequently made this metal one of the most important metals used today in technology. Zinc is a component of many alloys, including brass, aluminum zinc alloy. Rolled zinc sheets with the addition of titanium are used for roofing. It is used in electrical cells and in the form of zinc compounds. Zinc oxide ZnO (zinc white) is produced from primary zinc and is used in the chemical industry, as an additive to paints and varnishes and as a filler and stabilizer for rubber and plastics. Zinc sulfate has strong anti-inflammatory properties. Although zinc has been used in medicine for thousands of years, it was not until 1957 that zinc was officially recognized as one of the essential micronutrients [15]. In industry, zinc is most commonly used to coat steel products to protect against corrosion. Coatings produced by the hot dip galvanizing (HDG) method are the oldest known method of producing anti-corrosion coatings, patented in 1836 [12], and currently the most economical and effective anti-corrosion protection.

The article presents the current state and development of primary and secondary zinc production, taking into account the global demand and consumption of zinc, and reviews the trends of changes in the supply and demand for zinc in the world over the last several decades.

2. Zinc Production, Demand and Applications

2.1. Zinc Production

The good properties of zinc and the growing demand for this metal result in a continuous increase in zinc production throughout the 20th and 21st centuries. Table 1 shows the amount of zinc production in the years 1871–1927. Until 1840, Germany was the world's leading producer of zinc [13]. In 1907, world production was 737,500 tons, of which the United States produced 31%, Germany 28%, Belgium 21%, Great Britain 8% and all other countries 12% [13]. During World War I, zinc production increased significantly, reaching more than a million tons (1,079,155 tons in 1916 and 1,094,888 tons in 1917, respectively). In the post-war period, zinc production fell by almost half (520,418 tons in 1921), which was caused by the economic crisis. In the 1920s and 1930s, a continuous increase in zinc production was observed, which in 1944 reached the level of about 2 million tons. The increase in zinc production at that time was associated with the coming conflict and the outbreak of World War II. After the war, zinc production steadily increased, exceeding 3 million tons in 1960, 4 million tons in 1965 and 6 million tons in 1975 [16]. This resulted from the post-war reconstruction and the progressing economic development of the countries.

Table 1. The volume of global zinc production in the years 1871–1927, worked based on [17].

Year	1871	1881	1891	1901	1911	1921	1925	1927
Production, thousand tons	153.07	287.9	400.7	562.6	987.1	520.4	1247.0	1444.1

However, the greatest increase in zinc production is observed in the 1990s and in the early 21st century. Table 2 shows the amount of zinc production in the years 1991–2015 (data taken from [18–26]). In 2015, global zinc production increased to 13.9 million tons, mainly due to an increase in production in China. Zinc production indicators are the following: mine production (production of zinc contained in ores and concentrates), refined zinc production (production of metallic zinc quantifying the amount of zinc processed in the rectification process) and zinc usage (including both refined zinc and zinc extracted from other sources). World zinc production in 2016–2022, presented by the International Lead and Zinc Study Group (ILZSG) (Table 3), show that over 13 Mt of refined metallic zinc is currently produced annually, of which over 12 Mt comes from mine production [27].

Table 2. The volume of global zinc production in 1991–2015, worked based on [18–26].

Year	1991	1995	2000	2005	2010	2015
Production, million tons	7.310	7.480	8.730	10.700	12.896	13.900

Table 3. World zinc production and usage in years 2016–2022, working out based on [28].

Year	2016	2017	2018	2019	2020	2021	January–September 2022	2022
Mine production, million tons	12.66	12.654	12.723	12.799	12.253	12.789	9.479	9.206
Refined zinc metal production, million tons	13.56	13.538	13.142	13.546	13.780	13.858	10.362	10.111
Zinc usage, million tons	13.67	13.998	13.722	13.788	13.286	14.048	10.463	10.154

The decrease in zinc production estimated for 2021 due to the instability and uncertainty of the rate of economic growth rate caused by the development of the pandemic and the increase in COVID-19 infections [18] did not, however, result in a decrease in refined zinc production (Table 3). However, government lockdowns and a drop in zinc prices after the outbreak of the global COVID-19 pandemic caused a decrease in mine production in many countries in 2021, especially in South America [19]. This year, in the period from January to September, a clear decrease in both mine production, refined zinc production and zinc usage was observed compared to the same period in 2021 (Table 3) [28]. It is estimated that world mine production will peak in 2024, exceeding 14 million tons. After this period, mining is likely to decline due to the deteriorating quality of ores and the depletion of zinc reserves [18]. Total global zinc reserves are estimated at around 250 million tons. Due to the relatively high demand for this metal, it has been calculated that zinc reserves will probably only last for the next 17 years [26]. Figure 1 shows countries with large reserves of zinc deposits. Australia has the world's largest zinc reserves (68 million tons), followed by China, Mexico, Russia and Peru [26].

Figure 2 shows the production of zinc from ores and concentrates in the years 1995–2020. Since 1995, there has been a continuous increase in mining in China. In 1995, about 12% of mine production was produced by China. Within 25 years, the extraction of zinc ores in China increased to 35% of global extraction, reaching the level of 4.2 Mt in 2020 [26]. The main producers of zinc from ores and concentrates are also Australia (11% of production in 2020), Peru (10%) and Mexico (5%) [19].

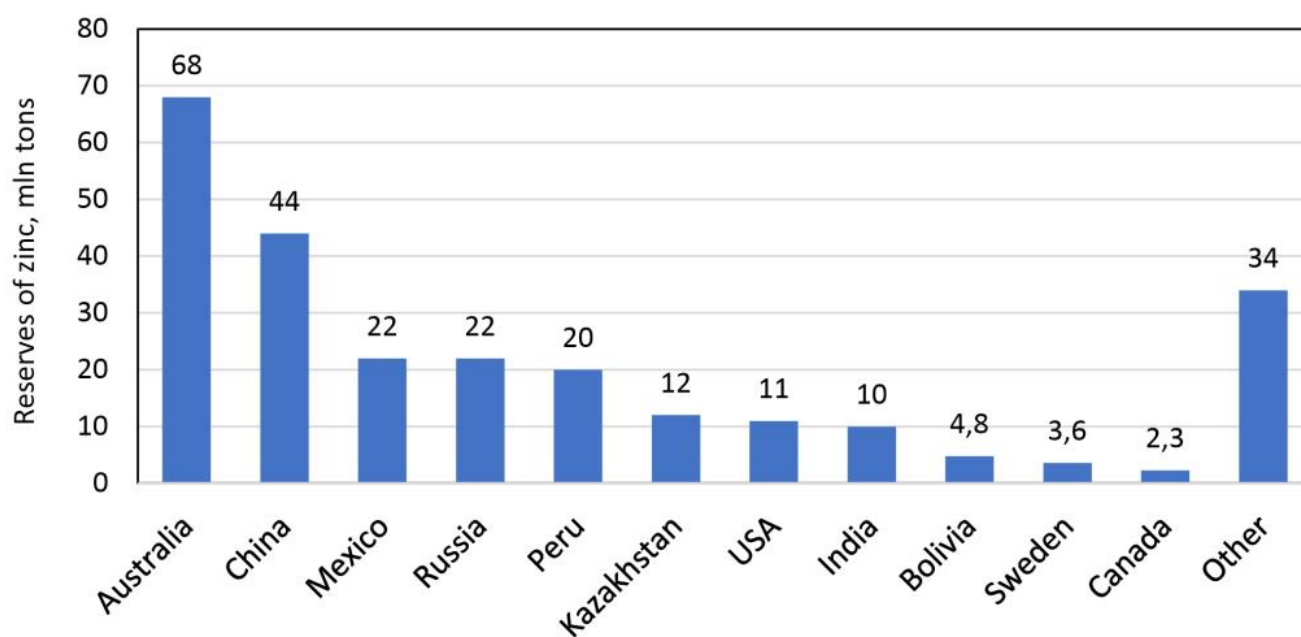


Figure 1. World reserves of zinc ore deposits in 2020, figure worked out based on data from [19].

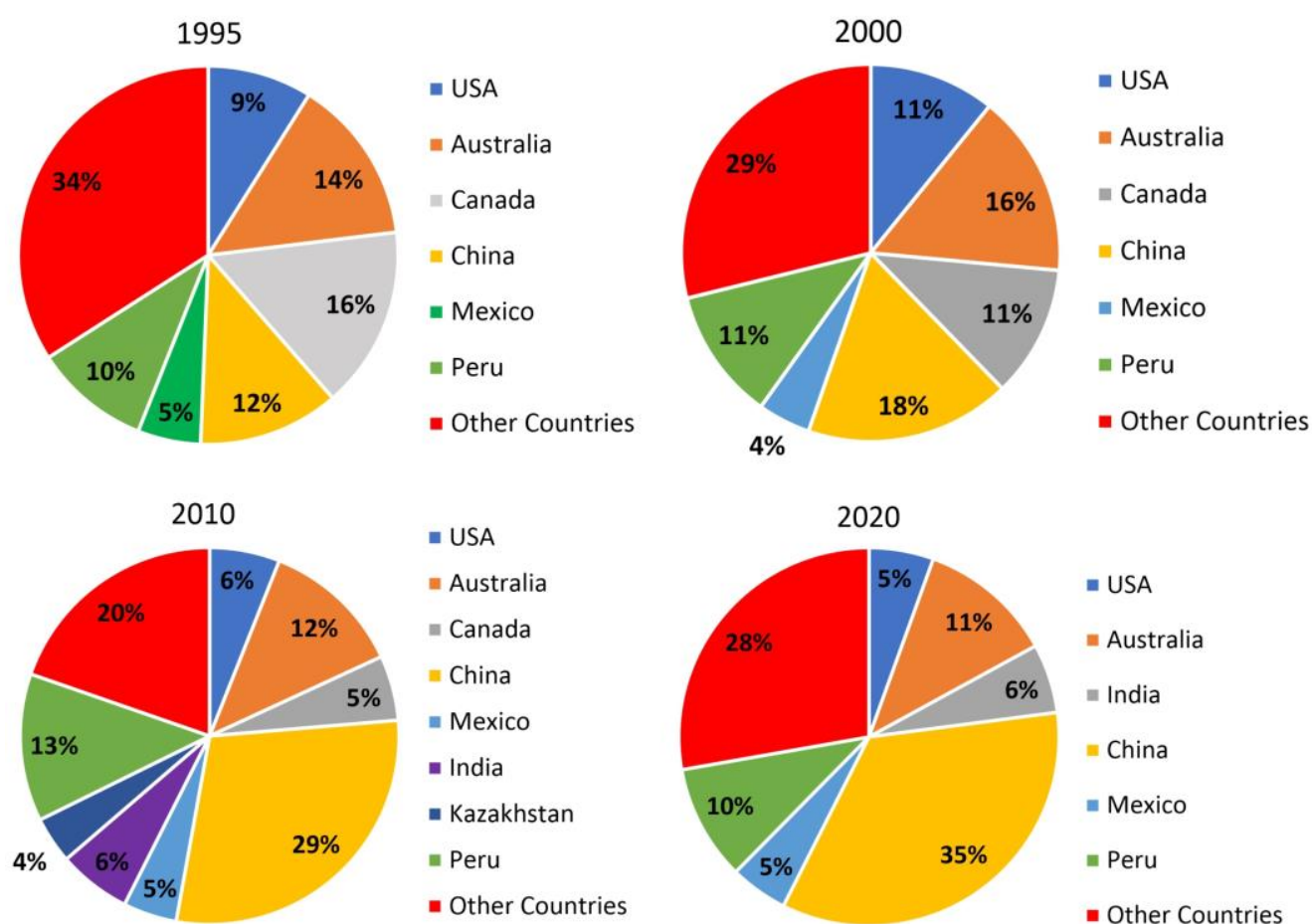


Figure 2. Zinc mine production in 1995–2020, figures worked out based on data from [19,29–31].

Table 4 shows the global producers of refined zinc [19,29–31]. In 2020, China’s share of total global zinc production was 46.9%. The next places are taken by South Korea with a share of 7% and India with 5% of global production. Refined zinc production in China increased from 550,000 tons in 1990 to 6425 thousand tons in 2020. Zinc production in China has increased by 1168% over the past 30 years.

Table 4. Refined zinc production by country, thousands of tones, worked out based on data from [19,29–32].

Country	1990	1995	2000	2005	2010	2015	2017	2018	2019	2020
Australia	303	337	489	508	507	490	471	490	437	469
Canada	592	720	780	805	691	683	598	620	655	671
China	550	1050	1957	2800	5209	6100	6144	5607	6236	6425
Finland	163	170	223	292	307	306	285	295	291	297
India	79	147	176	293	701	822	792	776	691	694
Japan	687	717	654	675	574	567	525	521	537	501
Kazakhstan	-	200	263	357	319	324	329	329	296	319
South Korea	257	250	473	645	750	935	970	1099	950	963
Mexico	199	223	337	360	322	327	327	336	393	365
Peru	118	165	200	164	223	335	321	334	357	348
Spain	253	325	386	546	517	491	510	511	511	511

Over several decades, a continuous increase and high volatility of the price of zinc has been observed. Even in the 1970s, the price of zinc was at the level of USD 260–270 per ton, reaching a historical record of USD 4442 per ton in November 2006 (Figure 3). In 2021, the price of zinc was USD 2989 per ton (1 September 2021) [33]. This price was practically half the value from the same period in 2020. It was estimated that the price of zinc in 2022 would fall to approx. USD 2400 per ton, with a slight increase in subsequent years [33]. However, the change in the geopolitical situation in February 2022 and the instability of the global economy meant that in April this year, zinc prices exceeded USD 4500 per ton. At the moment (December 2022), the price of zinc is USD 3200 per ton [34].

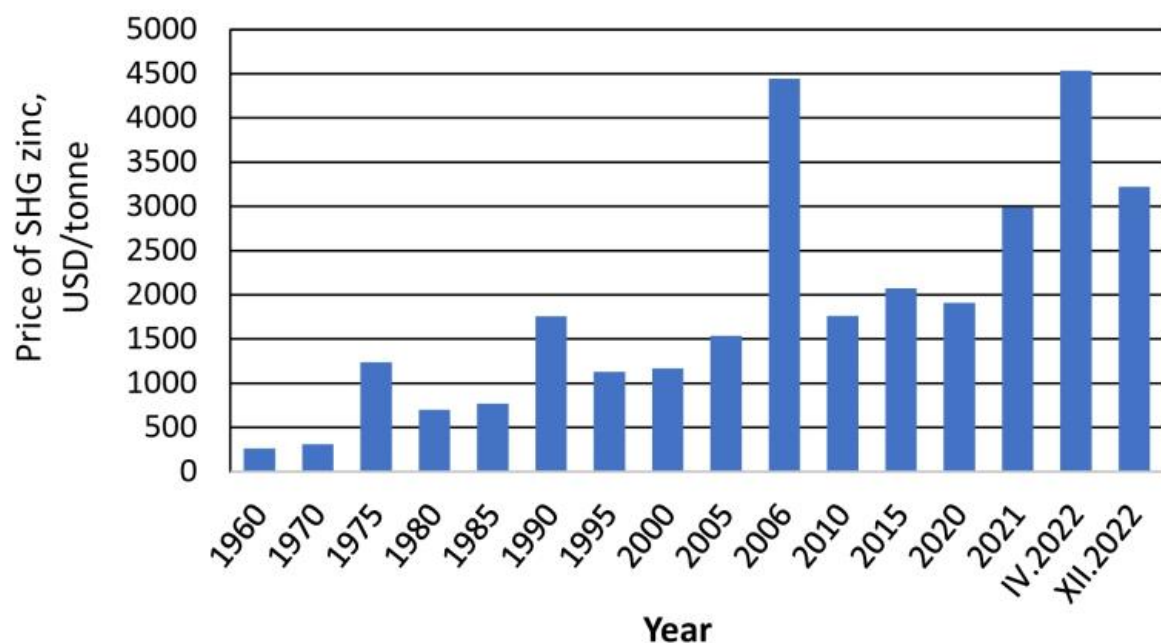


Figure 3. Zinc price in 1960–2022, figure prepared based on data from [32,33].

2.2. Application and Demand

Zinc usage in 2015–2022 was presented in Table 3. In 2016, the demand for zinc exceeded 13.67 million tons, reaching even 14 million tons in 2021. However, the year 2022 resulted in a decrease in the demand for zinc due to the downturn in the economy related to the lockdown and the effects of COVID-19. Although, according to the ILZSG, global zinc consumption exceeded production in the first 10 months of 2022. Therefore, annual zinc consumption also includes zinc from secondary or recycled sources, such products are collected and processed based on scrap availability, metal composition (e.g., purity, alloy, etc.) and ease of processing [27].

Zinc is now the fourth most used metal in the world after iron, aluminum and copper. It has strong anti-corrosion properties. Demand for zinc is mainly driven by the production of galvanized steel, which is widely used in many industrial sectors. As a result, about 50% of the currently produced zinc is used to produce anti-corrosion coatings by hot dip galvanizing method (Figure 4). About 1/3 of zinc production is used for the production of alloys. This application includes both zinc and aluminum casting alloys (approx. 17%) as well as zinc used as an alloying additive, mainly in brasses and bronzes (approx. 17%). The third significant application of zinc is the production of chemical compounds, including the most important in terms of the production volume of zinc oxide (6%). A similar share (6%) is the production of zinc semi-finished products, of which zinc anodes used in electrochemical corrosion protection and rolled zinc sheets with the addition of Ti are the most important for production [33,35].

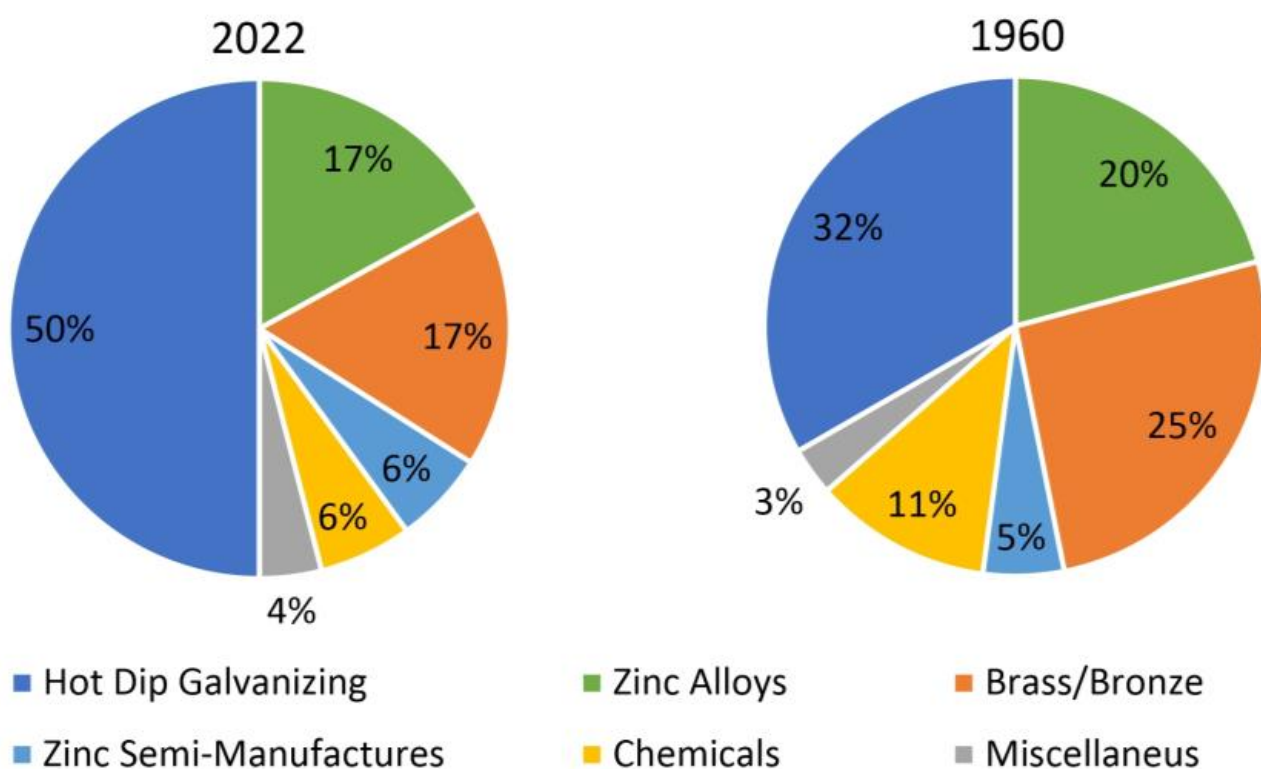


Figure 4. End use zinc consumption distribution in 1960 and 2022, figure worked out on data taken from [28].

Hot dip galvanizing technology has been dynamically developing over the last few decades. Although this process has been known for over 150 years (in 1836, Sorel patented the hot dip galvanizing process), the consumption of zinc for the hot dip galvanizing process is still increasing. In 1960, only 32% of global zinc production was used for the production of coatings (Figure 4b). Taking into account the global production of zinc in 1960 at the level of 6.8 million tons and over 13 million tons in 2021, this is a

significant increase in the consumption of zinc, mainly by the galvanizing industry. Zinc coatings obtained by the hot dip method are currently the most effective and economical anti-corrosion protection. According to statistics, the demand for this type of corrosion protection is constantly growing. In 2019, over 8.1 million tons of structural steel were galvanized in Europe and only compared to the data from 2018, an increase in production by nearly 1% was recorded [36]. In North America, in 2019, 4.9 million tons of steel were galvanized, which gives an approx. 10% increase in the production of galvanized products compared to 2014 [37]. However, by far, the largest HDG market in the world is China. The estimated production of galvanized steel in 2017 was 44 million tons, including 25 million tons of structural steel, 15 million tons of pipes and 4 million tons of small assortment (bolts, nuts, etc.). Zinc consumption for galvanizing in China is currently 58.2% of the country's total zinc consumption, which is higher than the world average (about 50%) [38]. It should be noted that the demand for galvanized products in China was about 200,000 tons of steel in 1982, about 300,000 tons in 1992 and about 9,000,000 tons of steel in 2002 [39]. These data show that in the last few decades, the amount of galvanized steel in China has been growing exponentially, reflecting the global increase in zinc consumption.

The galvanizing industry has a decisive influence on shaping global zinc production and market. Commonly used for galvanizing in the 80 s of the last century, metallurgical zinc Good Ordinary Brand (GOB) with a lower purity of 98.5 wt.% contained up to 1.5 wt.% impurities, including up to approx. 1.4 wt.% Pb [40]. The galvanizing bath always contained lead with a content close to the solubility limit in liquid zinc of 1.2 wt.% [41]. Lead was willingly used as an alloying additive to the bath because it lowers the surface tension of liquid zinc and improves the castability of the bath [42]. This results in better zinc flow from the surface of the product, which results in reduced zinc losses and its lower consumption during the galvanizing process. However, the presence of Pb in the bath is very controversial due to its negative impact on the environment and human health [43,44]. In the 80 s of the last century [40], the production of Special High Grade (SHG) zinc with high purity of 99.995 wt.%, in which the level of all impurities does not exceed 0.005 wt.%, significantly increased [45]. The use of GOB zinc for galvanizing systematically decreased, and SHG zinc took its place. Currently, practically only SHG zinc is used for galvanizing in Europe. Although Pb is sometimes added to baths, its content does not exceed 0.4–0.5 wt.% [46]. However, most galvanizing plants reduce or completely eliminate the addition of Pb to the bath, replacing it with the addition of Bi [47] or BiSn [48,49].

The specificity of the hot dip galvanizing process causes the efficiency of zinc used to be lower compared to other areas of zinc production and consumption. Zinc consumption depends not only on the thickness of the coating but also on the losses resulting from the specificity of the technology, i.e., the formation of hard zinc and galvanizing ashes, oxidation of the bath surface and formation of precipitations of solidified zinc. Studies have shown that one ton of zinc used in the hot dip galvanizing process generates 147.6 kg of hard zinc and 139.3 kg of zinc ashes. The average zinc content in hard zinc ranges from 94 to 96 wt.%, while the average zinc content in galvanizing ashes ranges from approximately 70 wt.%. This means that for each tone of SHG zinc delivered to the galvanizing plant, on average, approx. 240 kg of zinc is ineffectively used to create waste in the form of hard zinc and zinc ashes [49]. These are, of course, by-products rich in zinc, which is the raw material for the production of secondary zinc.

The main areas of application of zinc are the following: construction and infrastructure (66%), automotive industry and industrial machinery (28%), consumer goods and electrical appliances (23%) and general engineering (7%) (Figure 5). It should be noted that both steel structures, infrastructure and car bodies are commonly protected against corrosion by hot dip galvanizing coating. This explains such a large share of these areas of application in the global structure of zinc consumption. However, in recent years, new directions for zinc applications have emerged. Agriculture may be a growing end market for zinc applications. Zinc is currently recognized, together with potassium, as one of the most intensive organic

fertilizers. It is predicted that China and India will be potential areas for the application of zinc-based fertilizers in the future [50].

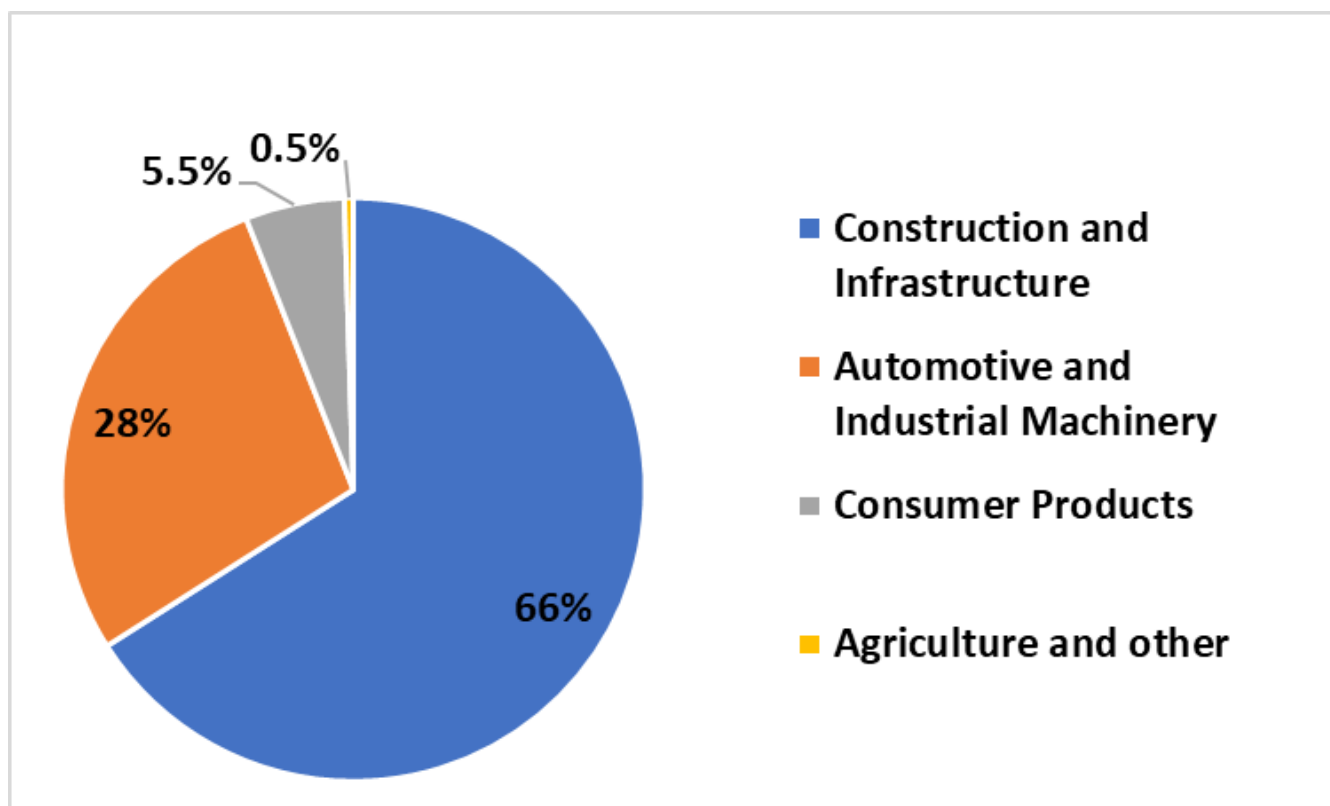


Figure 5. Zinc end use by applications in 2018, figure prepared based on data taken from [50,51].

3. Zinc Production from Primary Resources

Of the many zinc minerals, only a few are of economic importance. Currently, up to 85% of all zinc production uses sphalerite (ZnS). Its world reserves are enough for several decades. Zinc oxide minerals are zinc carbonates, including smithsonite and hydrozincite and the zinc silicates hemimorphite and willemite. Zinc oxide ores are generally less of a metallurgical and environmental problem than zinc sulphide ores due to the absence or relatively low amounts of elements such as arsenic, cadmium, lead and sulfur. Due to the depletion of sulphide ores and the reduction of sulfur emissions during the technological process, there is an increasing interest in oxide ores, e.g., carbonates and silicates [52,53]. The first stage of obtaining zinc from such ores is the production of a concentrate by flotation or by gravity method. If sulphide or oxide raw materials are processed, an average SO₂ content of 5% is obtained in the waste gases, and these gases are used in the sulfuric acid plant. When processing oxide-type raw materials, the SO₂ content in the flue gas is too low (0.3–0.5 wt.%) to be used in the sulfuric acid plant, so the gases must be treated in a different way.

The next stage is the processing of the concentrate by pyrometallurgical or hydrometallurgical means. The use of the pyrometallurgical path is not suitable for the processing of low-grade oxide ore due to environmental pollution, high capital expenditures and significant energy consumption [54,55]. Pyrometallurgical methods have various disadvantages, including high energy consumption, significant capital investment and the production of harmful greenhouse gases. The advantage of hydrometallurgical processes is that, on a small scale, the process can be economical due to low capital and operating costs and the recovery of valuable metal-containing products. In addition, the hydrometallurgical processing of zinc minerals has some environmental benefits. Figure 6 presents the available methods of processing zinc ores in the world, while Table 5 presents the characteristics

of the main processes used for the processing of zinc ores. Primary zinc is supplied to the market in various qualities, with the highest quality being special high-grade (SHG) zinc or Z1, which contains 99.995 wt.% zinc, followed by Z2 (99.99 wt.%), Z3 (99.95 wt.%), Z4 (99.5 wt.%); while the lowest quality good ordinary brand (GOB) or Z5 is around 98.5 wt.% purity. In addition, this zinc contains such impurities as Pb up to 1.4 wt.%, Cd up to 0.005 wt.%, Fe up to 0.05 wt.%, Sn up to 0.001 wt.%, Cu up to 0.002 wt.% and Al up to 0.001 wt.%. Simultaneously, secondary zinc grades are divided into the following three categories: ZSA (obtained mainly by zinc-bearing process scrap, e.g., Zn ashes)—98.5 wt.% with impurities such as Pb (1.3 wt.%), Cd (0.02 wt.%), Fe (0.05 wt.%) and Al (0.05 wt.%); ZS1 obtained mainly by recycling of scrap containing 98 wt.% Zn and ZS2 containing 97.5% Zn.

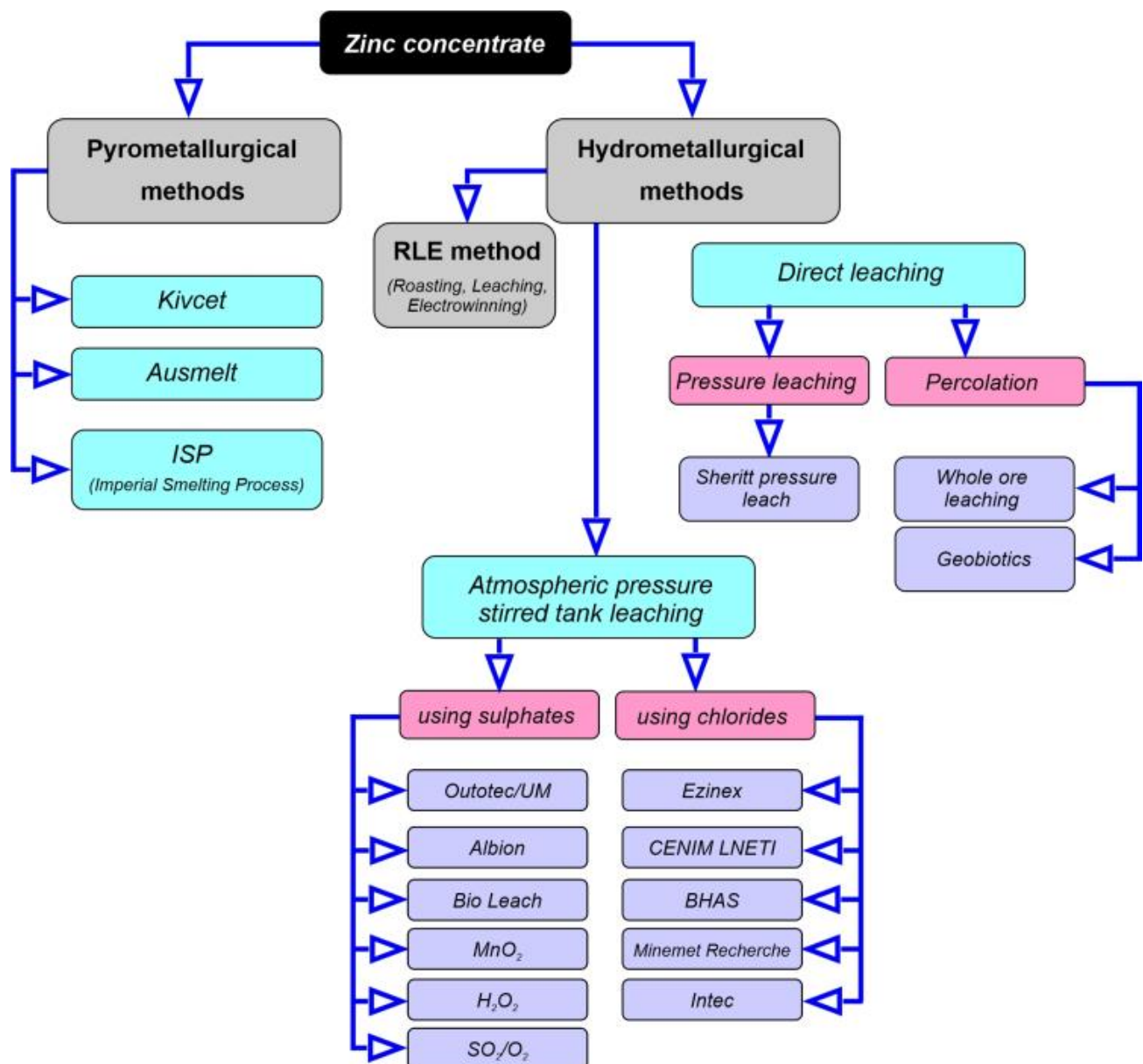


Figure 6. Available methods of processing zinc ores, figure prepared based on data taken from [56,57].

Table 5. Characteristics of basic methods of obtaining zinc from ores and concentrates, worked out based on data from [58–67].

Process	Characteristics
Roasting– Leaching– Electrowinning (RLE)	Conventional zinc hydrometallurgical technology, which consists of five main stages, i.e., roasting, leaching, solution purification, electrowinning and casting; the ore after enrichment becomes zinc concentrate, which is then converted into zinc oxide in the following roasting process: $\text{ZnS} + 0.5\text{O}_2 = \text{ZnO} + \text{SO}_2 \quad (1)$ In the leaching process, the oxidized concentrate ores are treated in a sulfuric acid solution to release zinc ions from the concentrate as follows: $\text{ZnO} + \text{H}_2\text{SO}_4 = \text{ZnSO}_4 + \text{H}_2\text{O} \quad (2)$ Due to the contamination and heterogeneity of the concentrate, other metal ions that are harmful to the electrolytic process also pass into the leaching solution, therefore, the solution is purified before the following process of electrolytic separation of zinc from the electrolyte: $\text{ZnSO}_4 + \text{H}_2\text{O} = \text{Zn} + 0.5\text{O}_2 + \text{H}_2\text{SO}_4 \quad (3)$
Atmospheric Direct Leaching (ADL)	A typical hydrometallurgical process, which differs from the RLE process by the elimination of the roasting process (the zinc sulphide concentrate is crushed into fine particles and fed directly to the leaching process), oxygen is blown into the leaching process to oxidize the zinc sulphide (the leaching reaction takes place at high temperature and using iron ions as a catalyst), sulfur is recovered from the leach residue by flotation.
Engitec Zinc Extraction (EZINEX)	EZINEX is a hydrometallurgical process, based on the electrolyte NH_4Cl, capable of producing zinc metal directly from raw ZnO, the first industrial scale EZINEX plant was designed to produce zinc directly from electric arc furnace (EAF) dust by Engitec in Italy in 1993; the basis of the process is a unique hydrometallurgical zinc recovery system, insensitive to typical impurities affecting traditional Zn production.
Zinc Pressure Leaching (ZPL)	Direct pressure leaching of zinc sulphide concentrates to produce zinc sulphate solutions suitable for zinc recovery by electrolytic leaching while oxidizing sulphide sulfur to its elemental form only, as follows: $\text{ZnS} + \text{H}_2\text{SO}_4 + \frac{1}{2}\text{O}_2 = \text{ZnSO}_4 + \text{H}_2\text{O} + \text{S}^0 \quad (4)$ Developed by Sherritt over 40 years ago and used on an industrial scale since 1981, the Zinc Pressure Leaching (ZPL) process can be easily integrated into existing zinc refineries using RLE technology, allowing these plants to increase zinc production or replace old or obsolete equipment.
Direct Zinc Smelting (DZS)	In the late 1990s, Outotec (formerly Ausmelt Ltd.) conducted research for BUKA Minerals Ltd. On the direct smelting of zinc sulphide concentrates using the Ausmelt TSL technology, this work led to the development of a two-stage smelting process; it is particularly well suited to the processing of low-grade concentrates containing significant amounts of iron and other gangue impurities such as MnO, SiO_2 and MgO.
Oxygen Flash Cyclone Electro Thermal Process (KIVCET)	Developed by the VNIITSVETMET Institute in Ust-Kamenogorsk, Kazakhstan, in 1985, consists of the following two stages: in the first stage, lead sulphide concentrate, zinc smelter waste, recycled dust, silica, limestone, fine coal and coke are introduced from the top of the reactor into reaction shaft; together with oxygen, lead, zinc and other metal sulphides are converted into metal oxides during heating; oxides, silica and limestone form half-molten slag, and the gas reaches up to 15% sulfur dioxide; the following reactions take place at this stage: $\text{PbS} + 3/2\text{O}_2(\text{g}) = \text{PbO} + \text{SO}_2(\text{g}) \quad (5)$ $\text{ZnS} + 3/2\text{O}_2(\text{g}) = \text{ZnO} + \text{SO}_2(\text{g}) \quad (6)$ $\text{PbS} + 2\text{PbO} = 3\text{Pb} + \text{SO}_2(\text{g}) \quad (7)$ In the second step, PbO and ZnO are reduced by adding coke; gaseous zinc can be recovered as metal in the condenser.
Imperial Smelting Process (ISP)	ISP is one of the most widely used smelting technologies that simultaneously smelt zinc and lead, consists of two sub-processes, lead-zinc sintering and metal smelting; unrefined lead is tapped from the bottom of the shaft furnace, while gaseous zinc is introduced into the condenser, where mixers with specifically shaped rotors spread the liquid lead over the condenser space; as a result of the contact of the shaft furnace gas stream with liquid lead intensive heat exchange and dissolving of zinc vapor in the lead takes place; the technology was developed in the middle of the last century in the UK to create a pyrometallurgical process for the continuous extraction of zinc, in addition to traditional raw materials such as lead zinc sulfide, secondary materials such as dust and sludge from metallurgical processes, for this reason, the simultaneous production of metallic lead is an advantage of the process, because the marking of most recycling materials shows, apart from zinc, also lead.

4. Zinc Production from Secondary Resources

Products containing zinc, e.g., galvanized steel, become a source of raw materials for recycling (this is the so-called old scrap). These products are collected and processed based on scrap availability, alloy composition (e.g., purity, etc.) and ease of processing [68]. Currently, more and more zinc is produced, and this entails the generation of many zinc-containing wastes at various stages of its production (new scrap). Table 6 presents the formation of new and old zinc scrap at different stages of zinc production, while Figure 7 shows the material cycle in zinc recycling.

Table 6. Sources and types of zinc scrap, worked out based on [68].

Scrap Source	Skimming—New Scrap	Scrap Type Finished Products —Old Scrap	Steel Dust —Old Scrap	Recovery Process
Brass/Bronzes	Yes	Yes	No	Remelting
Zn–Al alloys	No	Yes	No	Remelting
Galvanizing	Yes	No	Yes	New scrap—remelting, old scrap—refining
Rolled zinc—Zn–Ti sheets	No	Yes	No	Remelting
Other	Yes	Yes	Yes	New scrap—remelting, old scrap—refining

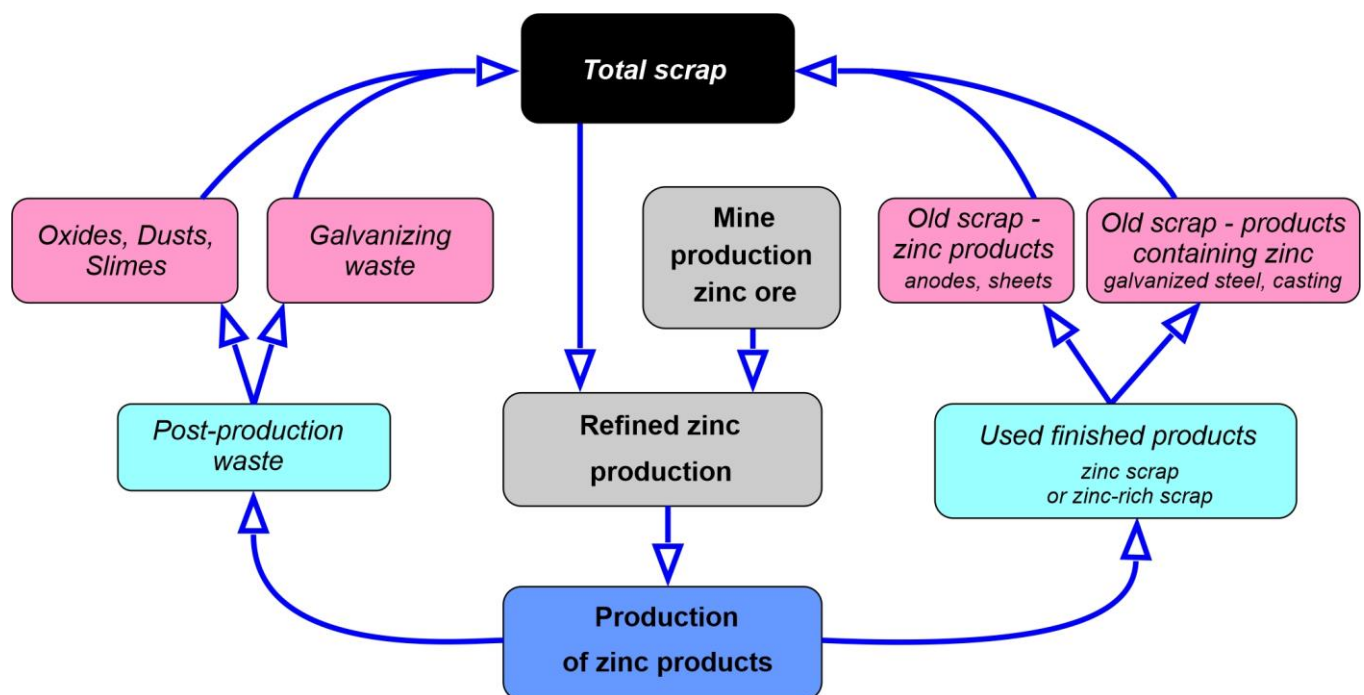


Figure 7. Material cycle in zinc recycling, figure prepared based on data taken from [69].

The primary energy Intensity of zinc production ranges from 49 to 55 GJ/tonne. Energy savings due to the recycling of steel (mainly in the case of galvanized steel) and zinc can range from 60 to 75% [57]. Worldwide, approximately 20% of zinc becomes new scrap in batch and continuous galvanizing processes.

Zinc concentrates have a relatively constant chemical composition, while the resulting zinc wastes contain zinc in varying amounts. Table 7 shows the characteristics of various zinc precipitations generated in the industry and during the production process. Galvanized steel is the main source of secondary zinc, both in the galvanizing process and

in the remelting of galvanized steel. The specificity of the hot dip galvanizing process causes the efficiency of zinc use is lower compared to other areas of zinc production and consumption. Zinc consumption depends not only on the thickness of the coating but also on the losses resulting from the specificity of the technology, i.e., the formation of hard zinc and galvanizing ashes, oxidation of the bath surface and formation of precipitations of solidified zinc. Studies have shown that one ton of zinc used in the hot dip galvanizing process generates 147.6 kg of hard zinc and 139.3 kg of zinc ashes. The average zinc content in hard zinc ranges from 94 to 96 wt.%, while the average zinc content in galvanizing ashes ranges from approximately 70 wt.%. This means that for each tone of SHG zinc delivered to the galvanizing plant, on average, approx. 240 kg of zinc is ineffectively used to create waste in the form of hard zinc and zinc ashes [49]. These are, of course, by-products rich in zinc, which is the raw material for the production of secondary zinc.

Zinc oxidation on the surface of the galvanizing bath creates zinc oxide (galvanizing ash) contaminated with flux decomposition products. The need to clean the surface of the bath before each immersion and the emergence of the charge generates a significant amount of galvanizing ashes. Ensuring a high-quality coating requires continuous cleaning of the bath surface and periodic removal of galvanizing ashes from it. During the collection of ashes, it is also inevitable that significant amounts of “pure” zinc will be removed from the surface. Galvanizing ashes are, therefore, a zinc-rich waste. During galvanizing, the iron is dissolved in the bath. The source of bath contamination with iron is galvanized products, but also the dissolving galvanizing kettle and flux contaminated with iron chloride. After the zinc bath reaches the state of saturation with iron (0.03 wt.% at 450 °C), excess iron reacts with liquid zinc and is released in the form of fine particles of intermetallic phases δ_1 (FeZn₇) or ζ (FeZn₁₃) forming the so-called hard zinc. When the galvanizing bath contains an Al additive above 0.14 wt.% (continuous galvanizing), the reaction of Al with dissolved iron leads to the formation of particles of the Fe₂Al₅Zn_x phase. Hard zinc, which can be identified as surface dross (mainly Fe₂Al₅Zn_x) and bottom dross (mainly δ_1 (FeZn₇) or ζ (FeZn₁₃) phase), hinders the galvanizing process and requires periodic removal—the surface dross is skimmed off by labor or machine at intervals, while the bottom dross can be removed when the operation is shut down. One novel efficient method called the supergravity method for recovering zinc from galvanizing dross has been proposed by the University of Science and Technology Beijing in China [70].

The hot dip galvanizing process also provides zinc-rich waste as a residue from the purification of finished products. Zinc thickening and drips formed on the surface are removed by mechanical grinding, and the removed zinc is re-melted. Zinc-rich wastes are also zinc sludges formed when wet fluxing is used. However, wet galvanizing is now much less frequently used.

Table 7. Characteristics of various zinc wastes generated in the industry and during the production process, worked out based on [57,71,72].

Waste	Source of Formation	Chemical Composition
Zinc ashes	Oxide surface on galvanizing bath	60–80% ZnO, 2–12% Cl, 0.2–1.5% Fe, <0.3% Al, small amounts of alloy additives for the bath Pb, Bi, Sn
Hard zinc	Particles of the intermetallic phases of the Fe-Zn system that fall to the bottom of the galvanizing bath	96% Zn, 4% Fe
Zinc slimes	Wet flux on the surface of the galvanizing bath	5.6% Zn, 48.1% ZnCl ₂ , 27.4% ZnO, 3.1 AlCl ₃ , 15.8% NH ₄ Cl and Fe and other oxides

Table 7. Cont.

Other waste from hot dip galvanizing process	Residues after finishing and cleaning products from infiltrations and thickenings of zinc	81% Zn, 16% ZnO, 0.3% Fe, small amounts of alloy additives Pb, Bi, Sn for the galvanizing baths
Brass skimming	An insoluble alloy that sinks to the bottom of the brass bath	41–42% Zn, 41–42% Cu, 1–2% Fe, 1–2% SiO ₂ , 0.1–0.5% Cl
Brass ashes	Volatile oxide surface on brass bath	20–30% ZnO, 4–8 Cu, 1.5–2.5 Fe, 0.25–20% SiO ₂ , 0.1–0.3% Cl
EAF kiln dust	Dust from the EAF furnace collecting above the bath	19.4% Zn, 24.6% Fe, 6.8% Cl, 4.5% Pb, 2.2% Mn, 1.2% Mg, 1.4% Si, 0.42% Cu, 0, 4% Ca, 0.3% Cr, 0.1% Cd
Waste after precipitation	Zinc metallurgical residues from purification of the electrolytic solution	9.5% Zn, 1.44% Co, 2.3% Fe, 5.27% Mn, 1.1% Cu, 0.16% Cd
Sludge from the washing process of rayon	Precipitated solution after washing rayon	18–40% Zn(OH) ₂ , 60–82% CaCO ₃ , others

Another important source of zinc is electric arc furnace (EAF) dust. It is estimated that the EAF furnace generates 15–25 kg of dust per ton of raw steel, the zinc content varies from 10 to 40%. The minimum zinc content necessary for the process of zinc recovery from steelmaking dust to be profitable depends on various factors, such as the proximity of the steelworks, energy costs, slag cost; however, it should be at the level of 15% [73]. Zinc is also contained in steelmaking dust from the converting process (BOF). However, the content of zinc in it varies between only 0.5 and 6%. This value is too small for the profitable recovery of zinc from these dusts. Zinc is not recovered from the BOF process dusts; the suggested solution, in this case, is to collect galvanized sheet scrap and send it to the EAF process or to dezincify steel scrap [74–76].

The hydrometallurgical production of zinc produces deposits and leaching and purification residues. In the production of rayon fiber yarn, zinc is used as a modifier for cellulose regeneration. After the rayon is made, it is washed and the solution contains 30–50 ppm of zinc, which precipitates in the form of zinc hydroxide [71].

Pyrometallurgical methods used to treat secondary zinc waste include the following: electrothermic retort processes (ERP), Imperial Smelting Process (ISP) and Waelz furnace. Hydrometallurgical processes include the following: molecular recognition technology (MRT), EZINEX process, Zincex process, CASHMAN process, sulfuric acid leaching process, chloride leaching process, chloride–sulfate leaching process, alkaline leaching process, crystallization and solvent extraction [77]. Table 8 presents the basic characteristics of the mentioned processes. One of the most commonly used processes for recycling today is the Waelz process. The recovery of zinc from this process is 91 to 93% [78], and the remaining 7–9% remains in the slag. This slag is directed to landfills. The product obtained in the rolling furnace is zinc oxide, which is the raw material for the process of obtaining metallic zinc in the ISP and solvent extraction–electrowinning processes, while up to 20% of the charge in the roasting–leaching–electrowinning (RLE) process. The use of zinc oxide as a feedstock in zinc smelters has been increasing in recent years; in 2016, it amounted to 878 thousand tons, while in 2019 already 1448 thousand tons [78]. This indicates an average annual increase in the use of ZnO at the level of 20% [36,38].

Table 8. Characteristics of metallurgical methods for processing secondary zinc waste [77,79–82].

Process	Characteristics
Molecular Recognition Technology (MRT)	The first commercial hydrometallurgical process for the treatment of EAF dust was launched in the USA (1995); the dust is leached with hot ammonium chloride to dissolve most of the zinc, lead and cadmium oxides in the dust; the leach slurry is filtered and unleached iron oxide containing zinc ferrite is filtered, washed and returned to the smelter or landfilled; the leaching solution is treated with zinc dust to precipitate the dissolved lead and cadmium as a precipitate, which is further separated into metallic lead and cadmium for sale; the pure solution goes to the crystallizer, where high-purity zinc oxide crystals are produced; the ammonium chloride solution is concentrated and recycled to the leaching process.
EZINEX	Process at Osoppo, Italy (since 1996), EAF dust is leached with ammonium chloride solution to dissolve Zn, Pb and Cd oxides; the leaching solution is filtered and treated with Zn powder to precipitate lead and cadmium; zinc is electrolytically separated from the purified solution, the spent electrolyte is recycled to the leaching stage; Fe-rich leach residue is dried, granulated with coal and recycled to EAF; no other by-products.
CASHMAN	A process adapted by American Metals Recovery Corp. for the purification of EAF dust, zinc which is not present in zinc ferrite is leached under pressure in a CaCl_2 solution; the leached solution is purified by precipitation using Zn dust to remove lead and cadmium; high purity ZnO precipitates from the purified solution; leaching residue is processed to recover residual zinc and produce iron-rich residue, the process uses pressure leaching, but zinc recovery is not very high.
Waelz process	The rotary kiln process for processing zinc dust is most often carried out in Waelz furnaces; zinc waste can be separated from iron due to high zinc vapor pressure.
Electrothermic Retort Processes	Developed by St. Joseph Mineral Company (in 1930), the possibility of smelting a wide range of zinc-bearing materials, including EAF dust, less efficient than hydrometallurgical processes, electrical resistance type furnaces are used in the process; the flow of current through the sintered ore and the coke charge generates the energy needed to melt them, the Zn vapors pass into the vacuum condenser, where zinc is obtained.
Zincex	A hydrometallurgical process using atmospheric leaching, solvent extraction and an electrolysis process, modified in the early 1970s, aimed at recovering Zn from complex Zn solutions with a high presence of impurities that are difficult to separate by conventional methods, it is now used commercially to process oxide ore Zn in Skorpion (Namibia), recycled in Akita (Japan), in Portovesme (Italy) and in Horsehead (USA).

All galvanized scrap, regardless of grade, is now recycled in the electric arc furnace. Currently, many methods are also used to recover zinc from the waste generated in the hot dip galvanizing process. An economic method of removing the zinc coating before re-melting the galvanized scrap is also being sought. This is not a new concept. Tin-plated steels are regularly subjected to a metal removal process prior to the recycling of tin-plated products. In fact, some original dezincification solutions were based on industrial processes for removing tin coatings [83]. Tin-coated steel is usually recycled in an alkaline detinning process, leaving the steel substrate to be re-melted.

The conducted studies on the recycling of galvanized steel scrap mainly concern alkaline dezincification, i.e., zinc dissolution by hot caustic soda (NaOH) to the form of sodium zincates (Na_2ZnO_2 and NaHZnO_2)—Figure 8a. Zinc is recovered electrolytically in the form of powder, while uncoated steel is readily used for re-melting [84]. Spontaneous alkaline dissolution of zinc (without heating or using an external electric current source) is thermodynamically possible but kinetically limited [85,86]. Dissolution will only occur when the zinc is in electrical contact with a metal with a lower hydrogen overpotential, such as platinum, iron, or nickel, or if a strong oxidizing agent is added. Recently, acid dezincification has been quite popular—Figure 8b. Typically very low concentrations of acid make the process safe, and the dissolution reaction occurs spontaneously, without the need for heating or the use of an external source of electricity. The advantage of using dilute acids is the complete dissolution of the zinc coating with little or no attack on the steel substrate, which is eventually recycled while the zinc is recovered from the solution either in metallic form or as a metal salt depending on the type of acid used.

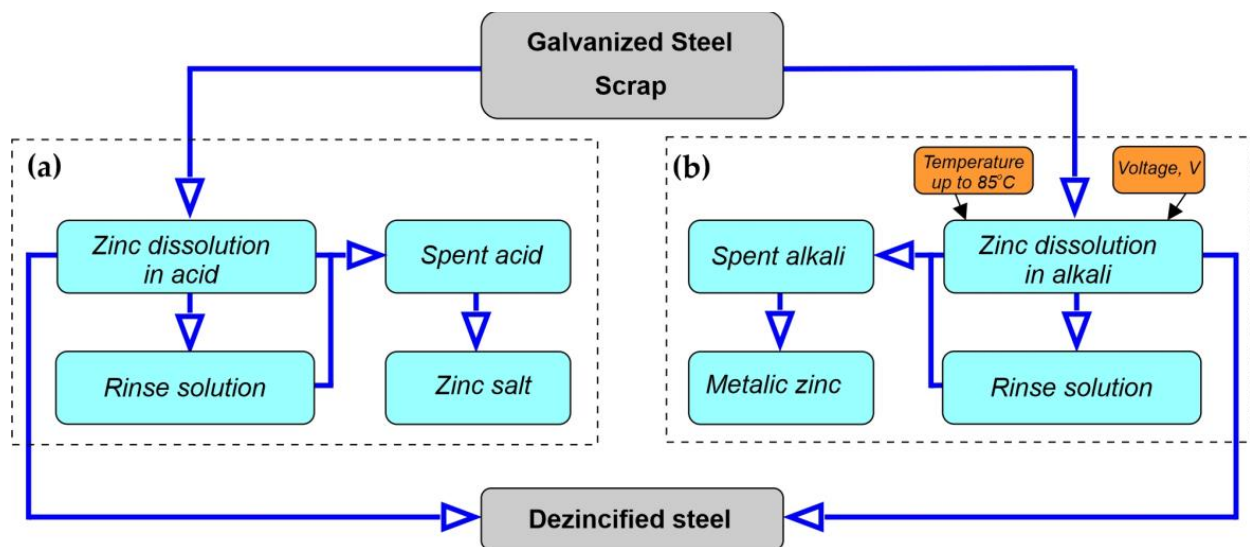


Figure 8. Scheme: (a) acidic and (b) alkaline dezincification of galvanized products.

The following reactions occur in the acid dezincification process:

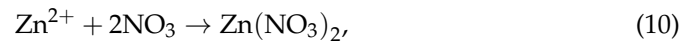
- Zinc dissolution:



- Hydrogen release:



- Formation of zinc salts:

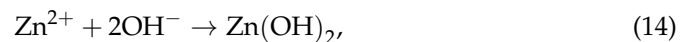


In the alkaline dezincification process, the following reactions take place:

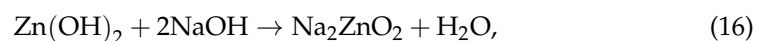
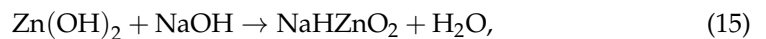
- Oxygen reduction:



- Formation of zinc hydroxide:



- Formation of zinc salts:



In the case of the acid dezincification process, it was found that more concentrated acids (more than 10%) tend to accelerate the dezincification rate but also have an intense effect on the dissolution of the steel substrate. Dilute acids (2% or less) reduce the rate of dissolution but tend to dezincify partially or even ineffectively [84].

To sum up, in hydrometallurgical processes, valuable metals with a high mass fraction can be obtained. The energy consumption of the processes is low due to their low temperature. Unfortunately, these methods require high corrosion resistance of the devices. Slag obtained after leaching is also problematic due to its complex composition, and it cannot meet the storage requirements of environmental protection law. Pyrometallurgical methods are also used for dezincification (e.g., in Japan, there are two plants based on this solution),

but they are much more expensive. They focus on steel scrap, and the recovery of zinc products is practically low [87]; what is more, these processes are highly energy-intensive and require large equipment.

Figure 9 shows the flow of recycled zinc, taking into account the hot dip galvanizing process and finished products withdrawn from circulation [88]. Currently, about 70% of the zinc comes from primary refining of zinc ores (including 10–15% from recycling sources), and about 30% comes directly from recycled zinc (accounting for 80% of the zinc available for recycling). The long life of galvanized steel products in the construction industry makes predicting their appearance in waste streams difficult.

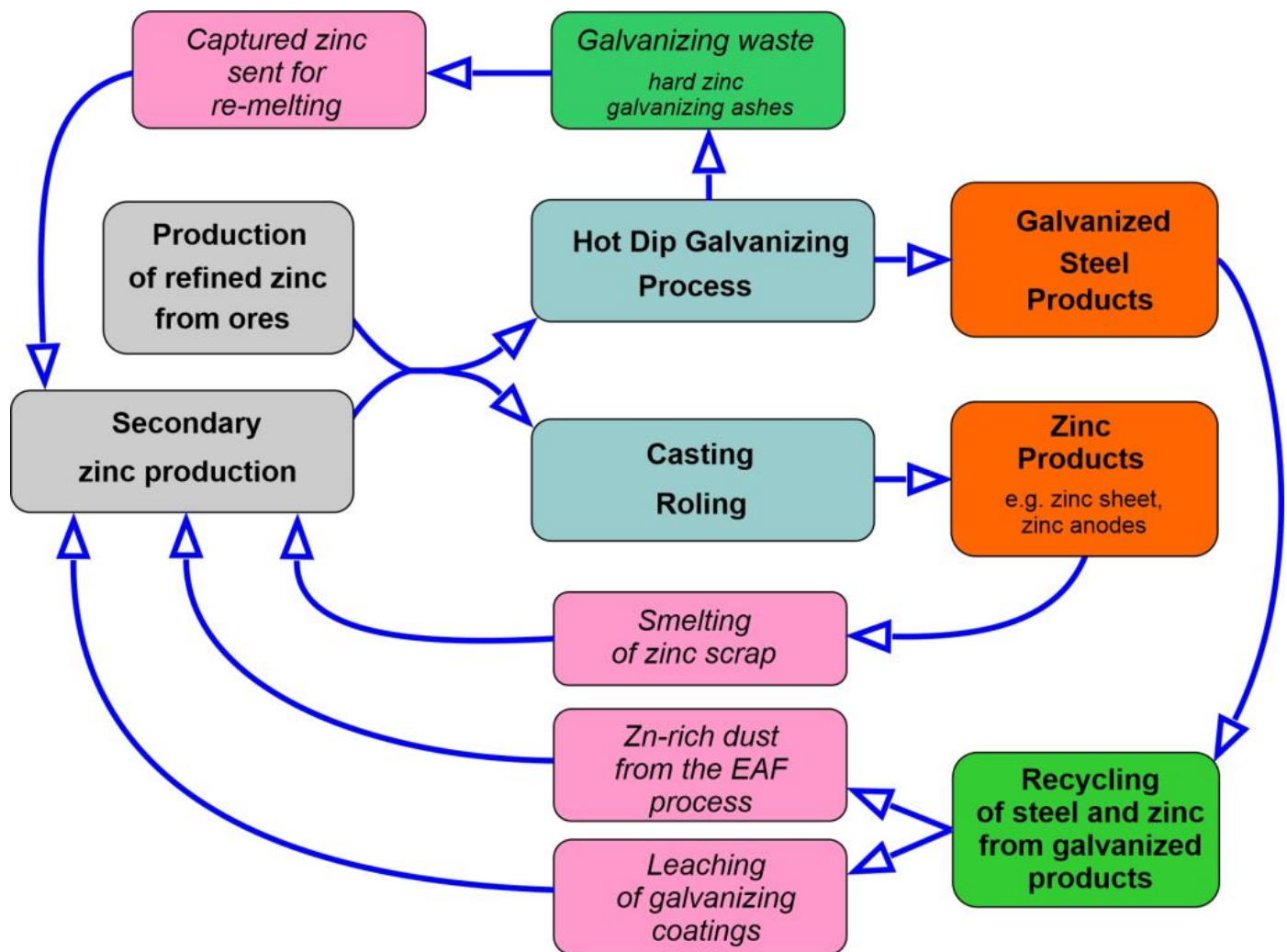


Figure 9. Recycling zinc flow, including the hot dip galvanizing process and finished products withdrawn from circulation.

In the case of zinc, the following two recycling rates are used: end of life (EOL) and recycled content (RC). The EOL indicator offers a very comprehensive approach by taking into account recycling efficiency, product lifetime and historical production patterns; quantifies the value of the zinc actually recovered at the end of the product's life ('old scrap') and recycled into new metallic zinc. It is estimated that around 45% of the available zinc at the end of the life of various zinc-containing products is recovered and actually recycled (Table 9). In developed regions such as Europe and North America, the EOL rate may be 50% or greater. For developing regions, the rate is 30–40% due to the lack of developed recycling networks and regulatory initiatives aimed at reducing industrial waste [71]. Recycled content RC is a measure of the recycled content in a product. The

recycled content for refined zinc is currently around 8% (scrap combined with concentrate as raw material in the smelter).

Table 9. Recycling process indicators, worked out based on [71].

Indicator	Description	Estimated Global Recycling Rate
Recycled content (RC)	Zinc scrap fraction (new and old) in the total use of metal in production	25%
Ratio of old scrap	Zinc fraction from old scrap in the general recycling loop	70%
EOL recycling rate	Fraction of recycled zinc in relation to the amount of zinc available at the end of its life	45%

Table 10 shows the production of zinc, taking into account the method of obtaining it. It can be seen that, over the years, more attention has been paid to the amount of recycled zinc. However, the lifetime of zinc-containing products is variable. In particular, this applies to galvanized products, the specificity of which uses zinc to extend their durability. The durability of zinc coating protection depends on the needs of the market and the application. Then the service life may be from 10 to 15 years in the case of, for example, the service life of cars or household appliances. These products are scrapped due to the wear of other elements and subassemblies, although the zinc in these products still fulfills its protective role. The situation is different in the case of anti-corrosion protection of steel structures and products operated in an atmospheric environment with different corrosive aggressiveness. The aggressiveness of the atmospheric environment depends on many factors, e.g., temperature, humidity, and content of aggressive components, i.e., chlorides, sulfur compounds, weather factors, etc. The aggressiveness of the natural atmospheric environment may change over time. Then the durability of galvanized elements ranges from several to even 100 years and is difficult to predict.

Table 10. Total zinc production broken down into primary and secondary zinc production and non-differentiated production in thousands of tons, based on data from [89–91].

Year	1991	1995	2000	2005	2010	2015	2017
Primary production, thous. tone	4370	4160	4330	4680	4810	12,600	12,700
Secondary production, thous. tone	376	345	348	298	279	409	447
Undistinguished production, thous. tone	2570	2980	4460	5770	7710	711	691

5. Summary

Zinc can be produced from primary raw materials by pyrometallurgical or hydrometallurgical methods. Pyrometallurgical methods are still used in different parts of the world but gradually lose their importance and are no longer used, e.g., in the EU for the treatment of zinc concentrates, except in Poland. The main factors determining this are the need for an additional distillation step in order to obtain high-quality zinc and the relatively low efficiency of zinc extraction. In hydrometallurgical methods, there are problems with the emission of residual sulfur dioxide, NO_x and acidic effluents and the release of metals such as arsenic, mercury and cadmium, and additionally organic pollutants. Therefore, emissions to air and water, waste management and energy considerations are among the key factors influencing the choice of techniques used in the processing of zinc-bearing ores.

Currently, around 30–35% of the zinc consumed annually comes from recycling. Production of zinc from secondary sources brings a number of measurable benefits, such as saving primary resources and fossil resources used to provide energy in primary mining processes, reducing zinc storage and losses (maintenance of landfills and increasing the amount of waste cost a lot), reclamation of waste, mitigation of environmental effects and health, and improving the economic efficiency of existing infrastructure. Dust, metal particles, chemicals and harmful gases are released into the environment during the zinc mining and refining process. Although companies try to keep emissions to a minimum, the process

still harms the environment. The recycling process is also safer and cheaper. Recycling rates are increasing with advances in zinc production and zinc recycling technologies. However, it is estimated that this level will not increase rapidly due to the large dispersion of zinc products and the problematic collection of zinc scrap.

For the recycling process, one of the problems is the service life of the products, which is relatively long for steel, e.g., bridges, and steel structures that are in constant use. At present, the service life of zinc-coated steel products is extended. The long service life of products, as well as changes in the corrosiveness of atmospheric environments at that time, make the life of products less predictable. Both in the case of zinc and steel itself, the amount of scrap for secondary production may change, and shortages are observed periodically. In this case, primary production from ores and concentrates is based. Both steel and zinc are 100% recyclable with no loss of chemical or physical properties. For steel, it is estimated that virtually 100% of all structural steel is recovered for reuse; the same index for zinc is over 80%. Galvanized steel can be easily recycled with other scrap steel in the electric arc furnace (EAF) steelmaking process. Zinc evaporates in the initial phase of the process and is collected in EAF dust, which is then recycled at specialist facilities and often returned to the production of refined zinc. More problematic are the dusts from the converting process (BOF), where the zinc content is up to 6%, which is below the profitability of their recovery. Currently, the International Zinc Association (IZA) has developed models to quantify zinc recycling rates to demonstrate the recyclability of products and the effectiveness of recycling programs. However, one proposed solution for galvanized products is to collect them, and use acid or alkali dezincification as a pre-treatment, and then direct the cleaned steel scrap to an electric furnace or converter.

The level of recycling of zinc from ashes and hard zinc after galvanizing is currently high, but there is still a problem related to the collection and sorting of used zinc or galvanized items. In the future, this will be a necessity in some industry segments, but at the same time offers opportunities to improve zinc recycling rates. The most obvious opportunity to improve recycling rates is in developing regions, where advanced recycling networks and infrastructure investments continue to expand. The International Zinc Association constantly monitors the efficiency of zinc recycling and on the basis of material flow analysis (MFA), characterizes the life cycle of products containing zinc in various applications. However, one of the problems is still the lack of regulations to encourage the collection and processing of scrap metal. Currently, with the high volatility of the price of this metal, as well as the dwindling natural resources of zinc in the earth's crust, this is a necessary course of action.

To sum up, the issue of zinc recovery from waste materials gives significant environmental and economic effects compared to primary production from ores. However, it faces also many problems related to the preparation of waste materials, the content of zinc in them, and the content of other metals in them, which results in solving the problems of complex structure and correlation of metal-containing phases or re-oxidation of non-ferrous metals after reduction. However, due to the increasing demand for zinc and the decreasing resources of this metal, the production of zinc from waste materials becomes a necessity, and the above-mentioned problems are important issues to be solved.

Author Contributions: Conceptualization, M.S. and H.K.; formal analysis, H.K. and M.S.; investigation, H.K. and M.S.; resources, H.K.; writing—original draft preparation, M.S.; writing—review and editing, H.K.; visualization, H.K.; supervision, M.S. All authors have read and agreed to the published version of the manuscript.

Funding: This research received no external funding.

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: Not applicable.

Acknowledgments: Not applicable.

Conflicts of Interest: The authors declare no conflict of interest.

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