

ZINC AND ZINC ALLOYS

1. Introduction

Zinc [7440-66-6] is a relatively active metal and its compounds are stable. Since it is not found free in Nature, it was discovered much later than less-reactive metals, such as copper, gold, silver, iron, and lead. In early times, the smelting of copper ores containing zinc resulted in brasses, which were known to the Romans before 200 BC. Later, brasses were made by heating copper with zinc oxide or carbonate and charcoal. The oldest piece of zinc extent is an idol found in a prehistoric Dacian site in Transylvania, which analyzed at 87.52% zinc, 11.41% lead, and 1.07% iron (1). Zinc smelting is thought to have originated in China, where it was known in the seventh century AD how to make malleable zinc. In India, zinc was produced from ore mined at Zawar before 1380. By the seventeenth century, zinc was imported into Europe from Asia and in 1743 a zinc smelter for zinc oxide ore was erected in Bristol, UK. By the early nineteenth century, zinc smelting was well established in Germany and Belgium. Zinc was first produced in the United States at the arsenal in Washington, D.C., in

1835, and by 1860 The New Jersey Zinc Company had well-established smelting operations at Bethlehem, Pennsylvania.

In 1758 in England, John Champion was granted a patent for making zinc from roasted zinc sulfide, the main ore of zinc. This route is still the principal method of production today. Commercial zinc metallurgy started with batchwise horizontal retorts, which have had many variations, and progressed to continuous vertical-retort processes. Although some of the latter are important today, electrowinning dominates the field, and the Imperial Smelting blast furnace for zinc–lead remains competitive.

The main application of zinc is to protect iron and other metals from corrosion. Zinc in contact with iron and other metals, as a coating or attached anode, corrodes sacrificially and protects the iron. Most commonly, zinc is applied in the molten state, ie, galvanizing, but is also applied either by electrodeposition or by various mechanical procedures using zinc dust or powder. Zinc dust paints are growing in importance (2). Another important use is in alloys for die casting. These alloys are used extensively because of their high quality and low cost. Brass and bronze products account for the third largest usage.

Two monographs on zinc are valuable general references on zinc technology (3,4). Furthermore, detailed descriptions of extractive processes, resource data, and environmental- and energy-related papers from symposia of the Metallurgical Society of the AIME are a rich source of information (5–10).

2. Occurrence

Zinc, like most metals, is found in all natural waters and soils as well as the atmosphere and is an important trace element in plant and animal life. Rocks of various kinds contain 20–200 ppm zinc and normal soils 10–30 ppm (average ~50 ppm) in uncontaminated areas. The average zinc content of coal is 33 ppm. Seawater contains 1–27 µg/L (median ~8 µg/L), and uncontaminated freshwater usually <10 µg/L.

Zinc ores are widely distributed throughout the world; 55 zinc minerals are known (11–13). However, only those listed in Table 1 are of commercial importance. Of these, sphalerite provides ~90% of the zinc produced today. Sulfide ores usually occur in the range of 2–12% zinc (average ~4%) as mined.

Table 1. Common Zinc Minerals

Name	Composition	% Zn
sphalerite ^a	ZnS	67.0
hemimorphite ^b	Zn ₄ Si ₂ O ₇ (OH) ₂ ·H ₂ O	54.2
smithsonite	ZnCO ₃	52.0
hydrozincite	Zn ₅ (OH) ₆ (CO ₃) ₂	56.0
zincite	ZnO	80.3
willemite	Zn ₂ SiO ₄	58.5
franklinite	(Zn,Fe,Mn)(Fe,Mn) ₂ O ₄	15–20

^aZinc blend, wurtzite.

^bCalamine.

Table 2. World Mine Production, Reserves, and Reserve Base^{a,b}

	Mine production		Reserves	Reserve base
	2003	2004		
United States	738	770	30,000	90,000
Australia	1480	1300	33,000	80,000
Canada	1000	1000	11,000	31,000
China	1650	2000	33,000	92,000
Kazakhstan	395	400	30,000	35,000
Mexico	460	420	8,000	25,000
Peru	1250	1400	16,000	20,000
other countries	2040	1810	59,000	87,000
World total (rounded)	9010	9100	220,000	460,000

^aWorld Resources: Identified zinc resources of the world are ~1.9 billion tons.

^bIn metric tons.

Source: U.S. Geological Survey, Mineral Commodity Summaries, January 2005.

The oxygen-containing ores in Table 1 are often found in richer deposits ranging up to 35% zinc, most commonly smithsonite and hemimorphite. They are thought to have originated from sulfide mineralization and are minor sources of zinc. However, in the beginning, the U.S. zinc industry was based on the deposit of franklinite, zincite, and willemite in Sussex County, New Jersey. Zinc deposits are classified as contact metamorphic, irregular and associated fissure fillings, vein, stratabound in metamorphic rocks, stratabound in carbonate rocks, strataform, and deposits formed by supergene enrichment of laterization (13). Carbonate rocks, eg, limestone and dolomite, are common host rocks of zinc ore.

Table 2 lists mine production, reserves, and reserve bases for the top seven countries together with a figure for all other countries combined. In this table, “reserve base” means that part of the zinc resource that meets minimum criteria for current mining practices, including grade, thickness, quality and depth. The reserve base includes both measured and indicated resources, and may include resources that are presently subeconomic. The term “reserve” refers to that portion of the reserve base that could be economically extracted or produced at the time of determination (14).

Table 3 lists mine production for the top three U.S. states, together with a combined figure for all other states. Alaska accounts for 88% of U.S. zinc mining production.

Recovery of zinc from recycled scrap in the United States has held steady in recent years at ~38% of total production, with the balance coming from domestic and foreign ores. In 2003, 116,000 metric tons of zinc were recovered, including steelmaking furnace dust, galvanizer’s dross and skimmings and ashes.

Zinc minerals tend to be associated with those of other metals; the most common are zinc–lead or lead–zinc, depending on the dominant metal, zinc–copper or copper–zinc, and base metal, such as silver. Zinc does occur alone, most often in the northeastern district, and here, as elsewhere, recoverable amounts of cadmium (up to 0.5%) are present. Other minor metals recovered from zinc ores are indium, germanium, and thallium.

Table 3. **Mine Production of Recoverable Zinc in the United States, by State**^{a,b}

State	(metric tons)	
	2002	2003
Alaska ^c	660,000	656,000
Missouri	41,800	39,100
Montana	10,300	15,200
Other ^d	41,900	27,800
<i>total</i>	<i>754,000</i>	<i>738,000</i>

^aData are rounded to no more than three significant digits; may not add to totals shown.

^bIn metric tons.

^cData based, in part, on publicly available information.

Table 4. **Leading Zinc-Production Mines in the United States in 2003^a**

Rank	Mine	Country and state	Operator	Source of zinc
1	Red Dog	Northwest Arctic, Ark.	Teck Cominco Alaska Inc.	Lead-zinc ore
2	Greens Creek	Juneau, Ark.	Kennecott Greens Creek Mining Co.	Zinc ore
3	Brushy Creek	Reynolds, Mo.	Doe Run Resources Corp.	Lead ore
4	Gordonsville	Smith, Tenn.	Zinifex Ltd.	Zinc ore
5	Montana Tunnels Tunnels Mining, Inc.	Gold ore	Jefferson, Mont.	Montana
6	Clinch Valley	Grainger, Tenn.	Zinifex Ltd.	Zinc ore
7	Buick	Iron, Mo.	Doe Run Resources Corp.	Lead ore

^aIn order of output.

Source: U.S. Geological Survey, Minerals Yearbook 2003.

A directory of world lead and zinc mines is contained in Ref. 15. A survey of world zinc production in Ref. 16 lists all primary and secondary zinc smelters.

Open-pit zinc mining is not common, since most mines are below the surface. The Kidd Creek Mine in Ontario, Canada, is a combination open-pit–underground mine. It is one of the richest deposits in the world with an estimated 62.5×10^6 t grading 7.08% zinc, 1.33% copper, and 151 g silver (17). Underground mining methods include room-and-pillar, shrinkage, cut-and-fill, and square set. In the United States, the seven leading mines out of the 16 operating are shown in Table 4.

3. Physical Properties

Zinc is a lustrous, blue-white metal, which can be formed into virtually any shape by the common metal-forming techniques, such as rolling, drawing, and

Table 5. Physical Properties of Zinc^a

Property	Value
ionic radius, Zn ²⁺ , nm	0.074
covalent radius, nm	0.131
metallic radius, nm	0.138
ionization potential, eV	
first	9.39
second	17.87
third	40.0
density	
solid, g/cm ³	
at 25°C	7.133
at 419.5°C	6.830
liquid, g/mL	
at 419.5°C	6.620
at 800°C	6.250
melting point, °C	419.5
boiling point, °C	907
heat of fusion at 419.5°C, kJ/mol ^b	7.387
heat of vaporization at 907°C, kJ/mol ^b	114.8
coefficient of thermal expansion, mm/(m·K)	
volume	8.9
linear, polycrystalline	39.7
thermal conductivity, W/(m·K) ^b	
solid	
at 18°C	113.0
at 419.5°C	96.0
liquid	
at 419.5°C	60.7
at 750°C	56.5
electrical resistivity, n/m	
polycrystalline	$R = 54.6 (1 + 0.0042 t)^c$
liquid at 423°C	369.55
heat capacity, J/(mol·K) ^b	
solid	$22.39 + 10^{-2} T^d$
liquid	31.39
gas	20.80

^aRef. 18.^bTo convert J to cal, divide by 4.184.^c $t = 0 - 100^\circ\text{C}$.^d $T = 298 - 692.7 \text{ K}$.

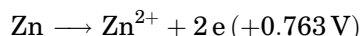
extruding. The hexagonal close-packed crystal structure governs the behavior of zinc during fabrication. Physical properties are given in Table 5.

Mechanical history, heat, and impurities greatly affect the mechanical properties. Pure zinc is ductile at room temperature and does not have a definite yield point as do most structural metals. Rather, it creeps under sufficient constant load. The impurities of commercial zinc and alloying metals are carefully controlled to achieve the desired mechanical properties.

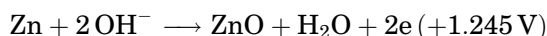
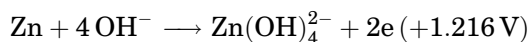
4. Chemical Properties

The most significant chemical property of zinc is its high reduction potential. Zinc, which is above iron in the electromotive series, displaces iron ions from solution and prevents dissolution of the iron. For this reason, zinc is used extensively in coating steel, eg, by galvanizing and in zinc dust paints, and as a sacrificial anode in protecting pipelines, ship hulls, etc.

In batteries, a zinc anode undergoes the oxidation reaction,



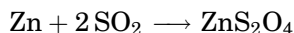
to provide a flow of electrons to the external circuit. For example, in the familiar dry cell, the zinc is oxidized to zinc chloride while manganese dioxide is reduced at the cathode. The alkaline zinc battery with manganese dioxide cathode uses potassium hydroxide electrolyte and forms zincate ions or precipitates zinc oxide at the anode:



Other alkaline primary cells couple zinc with oxides of mercury or silver and some even use atmospheric oxygen (zinc–air cell). Frequently, zinc powder is used in the fabrication of batteries because of its high surface area. Secondary (rechargeable) cells with zinc anodes under development are the alkaline zinc–nickel oxide and zinc–chlorine (see BATTERIES).

The capability of zinc to reduce the ions of many metals to their metallic state is the basis of important applications. However, metals are removed from zinc solutions by displacement with finely divided zinc before winning by electrolysis. Gold and silver are displaced from cyanide leach solutions with zinc and the following metals are similarly recovered from various solutions: platinum group, cadmium, indium, thallium, and sometimes copper.

Zinc hydrosulfite (zinc dithionite) is a powerful reducing agent used in bleaching paper and textiles; it is prepared from zinc dust and sulfur dioxide:



Another hydrosulfite reducing agent is zinc formaldehyde sulfoxylate, $\text{Zn}(\text{HSO}_2\text{CH}_2\text{O})_2$ (see ELECTROCHEMICAL TECHNOLOGY; ELECTROPLATING).

Pure zinc displaces hydrogen from acidic solutions slowly because of its high hydrogen overvoltage. This fact allows zinc to be electrodeposited by reduction from highly purified acidic solutions with only slight evolution of hydrogen. Surface amalgamation with mercury is useful in alkaline-battery applications because it increases the hydrogen overvoltage and reduces hydrogen gassing. Conversely, some metals reduce overvoltage and increase the rate of hydrogen evolution. Zinc dust, because of its high surface area, must be kept bone dry to avoid slow displacement of hydrogen from water. Massive zinc, on the other hand, reacts with steam rapidly $> 350^\circ\text{C}$.

Oxidizing elements, such as oxygen, sulfur, and halides, react with zinc at room temperature in the presence of moisture, but do not in its absence. At higher temperature, the reactions can be vigorous even when dry. For example, a powdered mixture of zinc and sulfur explodes if warmed and zinc reacts rapidly with oxygen at 225°C. Atmospheric corrosion of zinc results in hydrated basic carbonates, $x\text{ZnO} \cdot y\text{CO}_2 \cdot z\text{H}_2\text{O}$, of variable stoichiometry which form a surface film.

Zinc does not react with nitrogen, even at elevated temperatures, but zinc nitride, Zn_3N_2 , forms with ammonia at red heat. Zinc sulfide, the most common form of zinc in Nature, is not reduced directly in commercial practice because of reactions of the zinc vapor during condensation. Rather, the sulfide is burned (roasted) to the oxide plus sulfur dioxide before reduction. However, zinc can be reduced to the metal at $\sim 1300^\circ\text{C}$ with carbon or iron.

In the Parkes desilvering process, 1–2% zinc is added to molten lead where it reacts with any gold, silver, and copper to form intermetallic compounds which float as crusts or dross that is skimmed (see LEAD AND LEAD ALLOYS).

5. Processing

5.1. Concentration. Zinc ores are too low in zinc content for direct reduction and must be concentrated. They are first crushed, usually underground, in jaw, gyratory, or cone crushers, and then ground to 75–150 μm (100–200 mesh) by ball or rod milling to a degree necessary to separate the zinc minerals from other minerals and gangue in later (qv). In some ores, the zinc and lead minerals are too intimately mixed to be separated by flotation and are separated by leaching for subsequent electrowinning or in the Imperial Smelting furnace (ISF). The beneficiation of zinc ores is usually more complex than for other nonferrous ores because of the diversity of minerals present. Not only are copper or lead often associated, but the sulfide ore is sometimes partially oxidized.

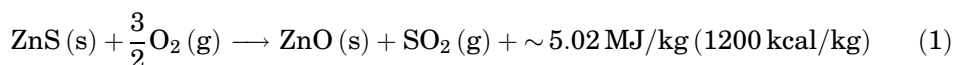
Beneficiation before grinding can be done by gravity or magnetic methods (19). Wetherill high intensity magnetic separators were developed by The New Jersey Zinc Company in 1896 to separate franklinite from their Franklin and Sterling ores. Jigging and tabling recovered the zincite and willemite. The concentrates were further upgraded to crude zinc oxide (20).

Zinc ores are generally floated at the mine (21). In the case of simple zinc sulfide ores, flotation is carried out by treatment with copper sulfate to activate the sphalerite causing it to be wet by the organic collector (eg, xanthate). The now-hydrophobic zinc ore particles attach themselves to the rising bubbles. Oxidized ore particles present must be sulfidized with sodium sulfide to be floated (22). Flotation produces concentrates that are ~ 50 –60% zinc. In mixed ore, the lead and copper are usually floated after depressing the sphalerite with cyanide or zinc sulfate. The sphalerite is then activated and floated.

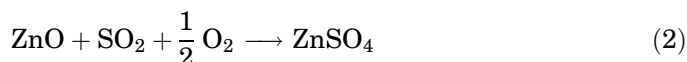
5.2. Roasting. Copper and lead sulfides are directly smelted, but not zinc sulfide. However, theoretical calculations are encouraging (23) and, if an efficient means of condensing zinc rapidly from 1600 K in the presence of carbon dioxide, sulfur dioxide, and steam can be devised, the process may be feasible.

The reaction of zinc vapor to yield zinc oxide or zinc sulfide presents the main difficulty.

The zinc sulfide in the concentrate is always converted to oxide by roasting. An exception is the direct leach process described below. The principal overall roasting reaction is strongly exothermic and provides excess heat that is recovered.



Under certain conditions, the oxide is sulfated:



In a usual roaster gas at equilibrium, the sulfate decomposes at $\sim 860^\circ\text{C}$, but it is difficult to avoid some sulfurization during cooling and indeed some plants require a degree of sulfation to maintain sulfate balance.

Another important reaction accounts for sulfur trioxide in the roaster off-gases and is a component of reaction 2.



Reaction 3 also occurs on cooling since the concentration of SO_3 is very low at roaster temperatures of 950°C and approaches zero at 1000°C . Another important reaction that occurs during roasting is the formation of zinc ferrite, $\text{ZnO} \cdot \text{Fe}_2\text{O}_3$, $> 650^\circ\text{C}$. Zinc ores contain 5–12% iron. Zinc ferrite forms solid solutions with other spinels, such as $\text{FeO} \cdot \text{Fe}_2\text{O}_3$, and therefore the zinc–iron compositions formed are of indefinite stoichiometry. Ferritic zinc is difficult to solubilize in hydrometallurgical leaching but several recovery processes are discussed below.

The sulfur dioxide of reaction 1 is cooled in a waste-heat boiler, freed from calcine, and converted to trioxide. The oxidation and conversion to sulfuric acid is conducted in a conventional acid plant.

For environmental and economic reasons, the early practice of roasting zinc sulfide and discharging the sulfur dioxide to the atmosphere gave way to plants where the sulfur dioxide is converted to sulfuric acid. Desulfurization takes place while the ore particles are suspended in hot gases. Called flash- and fluid-bed roasters, these processes are described below. Some plants use combinations of roasters and sintering for desulfurization.

Multiple-Hearth Roasters. The circular types consist of a series of hearths arranged vertically in such a way that the ore entering the top is rabbled and dropped down from hearth to hearth, until it is completely oxidized. The hearths are usually stationary and the plows revolve, such as in the Wedge, Herreshoff, Ord, Skinner, and other roasters (24). In other furnaces, the hearths revolve and the rabbles are fixed, eg, the deSpirlet and its modification, the Barrier.

A conventional circular-wedge roaster consists of a brick-lined steel shell with hearths arched gently upward from the periphery to a central shaft. The brick hearths may number from 8 to 16 and are ~ 1 m apart. The central steel shaft (~ 1.2 m in diameter) revolves at 1 rpm or less carrying two rabble arms per hearth. These rabbles, cooled with air or water, plow the ore from the outside to the center of the hearth where it is dropped to the next hearth for plowing in the opposite direction. The calcine thus proceeds to the bottom where it is dropped into a conveyor. The sulfide sulfur at this point is $\sim 3.5\%$ (25).

The uppermost hearth serves to dry the damp ore in the hot ($\sim 500^\circ\text{C}$) gases exiting the top of the toaster. These gases may contain up to 15% of the total crude oxide and up to 6% sulfur dioxide, high enough to be fed to a sulfuric acid plant. In some pyrometallurgical operations, desulfurization is continued in a sintering step.

Multiple-hearth roasting offers ease of operation, ability to handle a wide variety of ores or blends, and little downtime. On the other hand, these furnaces are no longer being built because of their high capital and labor costs, relatively low sulfur dioxide off-gas, need for added fuel, and marginal opportunity for waste-heat recovery.

Flash Roasting. As more and more zinc concentrates were produced by flotation, which requires finely ground ore, more rapid roasting was possible. Instantaneous oxidation was noted in multiple-hearth furnaces when particles were dropped from one hearth to another. The Consolidated Mining and Smelting Company of Canada (Cominco, Ltd.) took advantage of this observation to develop the flash or suspension roaster at Trail, B.C., Canada, in the early 1930s (26). An 8-m Wedge roaster with eight hearths was modified by removing all but the top two and bottom two hearths. Ore, fed to the top, is dried and then removed for grinding. After classification, it is conveyed back to the roaster where it is blown into the central chamber in a turbulent fashion using high pressure air jets. Oxidation occurs at $\sim 1000^\circ\text{C}$ and $\sim 40\%$ of the product falls to the bottom hearths. This coarser material is further desulfurized as it is rabbled out of the roaster. Some or all of the dust leaving with the gas stream is usually returned to the bottom hearths for further oxidation or decomposition of sulfate. The dust is removed from the gas by means of a cyclone following the waste-heat boiler. An electrostatic precipitator, wet scrubber, and dryer (sulfuric acid tower) clean up the gas before it passes to the acid plant.

New flash roasters dry on the bottom hearth; the ore is introduced in two opposed burners for increased turbulence (27). Such roasters with combustion chambers of 8–9 m high are capable of dead roasting (sulfide removal to $<0.5\%$) over 300 t of zinc concentrates per day with 10% sulfur dioxide in the off-gas.

The flash roaster is flexible in handling various flotation concentrates and reaching the degree of desulfurization desired, ie, 0.5–3.0% sulfate sulfur. Waste heat is easily recovered. However, grinding and rabbling must be done mechanically.

Fluidization Roasting. Fluid-bed roasting offers the advantages of reduced machinery, high throughput, good heat recovery, and rich sulfur dioxide off-gas (28,29). Most electrolytic zinc plants use fluid-bed roasting because of the ease of controlling the temperature to achieve proper sulfide and sulfate levels.

Compared to flash roasting, zinc leachability is better and sulfation is increased while the formation of zinc ferrite is minimized.

Slurry Fed. Dorr-Oliver, Inc., pioneered fluidization roasting and developed their FluoSolids process originally for treating arsenopyrite gold ores. The reactor (30) for roasting up to 155 t of concentrates per day is an insulated cylinder of brink-lined steel construction and with a conical bottom 9.5 m high with a diameter of 6.3–7.5 m. The windbox is separated from the reaction chamber by a distribution plate containing 780 nozzles designed to keep calcine from falling into the windbox. Fluidization air is supplied at 20,000 m³/h at 34.3 kPa (257 mmHg), ie, 30% excess over stoichiometric. In operation, the bed is 1.5 m deep and at 1.5 kPa (11 mmHg), under a slight positive pressure.

After start-up, the temperature is raised to the bed ignition temperature of 900°C. The feed slurry at 80% solids is pumped from an agitated tank and injected by atomization with compressed air. Evaporation of water from the slurry, or added supplementally, controls roasting at 900°C. The coarse calcine (40% of total) exits the top of the bed and flows to an evaporative cooler followed by cyclone and bag filter. The gases carry 60% of the solids to a waste-heat boiler where 15% of the total calcine is collected. Cyclones recover 40 and 5% is picked up by an electrostatic precipitator. The gas at this point is ~10% sulfur dioxide. The collected calcine is screened and the coarse fraction (>2 mm) is hammer-milled before being sent to leaching in the electrolytic plant.

The coarse calcine cooler operates at 300°C, while the waste-heat boiler cools the gas to 350°C. The tubes in the boilers have a chain-shaking arrangement operated by pneumatic hammers. Steam production is 0.78 kg/kg of dry concentrate. The only trouble with dust reported is in the connection between the reactor and waste-heat boiler. It is necessary to cool the gas stream quickly to avoid sulfation, but even so the carry-over calcine contains on the order of four times more sulfate than the coarse overflow. In this plant, the composite calcine is 0.1% sulfide and 2.2% sulfate sulfur.

A similar FluoSolids roaster handles 155 t/day of zinc concentrates through a roaster that is 1 m higher than standard (31).

The Dorr-Oliver slurry-fed roaster allows easy introduction of the concentrate, relatively low dust carry-over, good sealing, and freedom from cooling coils in the bed. It is usually operated at negative pressures to avoid sulfur dioxide and dust leakage but the in-leakage of air causes sulfation which may be undesirable. A temperature >900°C aids desulfurization by reducing carry-over; ie, the higher temperature induces particle sintering and agglomeration which diverts more of the calcine to bed overflow where it avoids sulfation. The principal disadvantage of the slurry-feed system is that the added water reduces the amount of heat that can be recovered.

Dry Fed. The dry feeding of fine concentrate to fluid-bed roasting was developed at S.A. Vieille-Montagne (now UMICORE) in Balen, Belgium, using a modified turbulent-layer process (BASF pyrites roaster). This process was sold to the zinc industry by Lurgi whose largest installation treats 800 metric tons of concentrates per day (32). In this roaster, unlike the Dorr-Oliver FluoSolids, so-called dry concentrates with 5–10% moisture are fed by mechanical belt slingers. In addition, the freeboard diameter is larger. Heat is removed

from the bed by cooling coils and adding water. The UMICORE roaster is the best for heat recovery and has a relatively low gas throughput.

The newest zinc plant in the United States at Clarksville, Tennessee, owned by Zinifex Ltd. of Australia, uses a UMICORE roaster (33). A single roaster treats 382 t of concentrate per day and recycles dross producing 333 t of calcine, while the acid plant produces 338 t of 100% sulfuric acid. The grate area of the roaster is 64.7 m² and normally would have five cooling coils in the bed. The low heat value (low iron sulfide) of the concentrates allows removal of three coils. Calcine leaves the roaster as bed overflow (~60%) or carry-over into the waste-heat boiler (~40%). The latter generates 18,160 kg of steam per hour at 3.9 MPa (~39 atm) pressure. Gases leaving the electrostatic precipitator contain 9.5% SO₂. Calcine from the roaster overflow and waste-heat boiler are cooled to ~100°C in a rotary-drum cooler and combined with cyclone and precipitator collects for dry ball-milling to <120 µm. Sulfur levels in the calcine are 0.25% sulfide and <1.5% sulfate. The clean, cool gas passes through a Norzinc mercury-removal tower (34) before entering the acid plant. Mercury reacts with soluble mercury(II) chloride to precipitate mercury(I) chloride, ensuring <1 ppm mercury content.

Canadian Electrolytic Zinc, Ltd., at Valleyfield, Quebec, uses two VM roasters to process 360 t of concentrates per day (35). Each roaster has 3300 tuyeres in its grate of 34 m² area, to fluidize a bed of 1 m depth; gas exits at 990°C. This plant was the first to use a water-cooled settling chamber in the waste-heat boiler for reducing the degree of sulfation. The gas exits the boiler at 320°C. An attempt was made to use spent electrolyte from the cells for roaster temperature control. This was designed to control the total sulfate in the plant, but it caused excessive bed agglomeration and increased sulfation.

Agglomerate Fed. Fluid-bed roasters of this type were developed in order to avoid the sintering stage in preparing feed for pyrometallurgical zinc operations where agglomerate strength and freedom from volatile components (sulfates, cadmium, etc) is essential.

The UMICORE smelter in Overpelt, Belgium uses hard pellets as a suitable feed for horizontal retorts (36). The MHO roaster, started in 1954, was the first to recover waste heat and was developed in collaboration with Dorr-Oliver. Concentrates and recycled fines are homogenized with sulfuric acid from scrubbing and pelletized to 0.5–4-mm size. The pellets are dried and fed to the rectangular roaster where the bed flow is longitudinal to the discharge port. The furnace is 5.5 m high inside. For 85% of the length, fluidization air is introduced and the balance of the bottom is an aperture where the pellets fall into a finishing bin. Crude pellets are less dense than calcine and tend to float in the upper portion of the 1-m-deep bed. Calcine enters the finishing bin at 980°C where incoming air completes the oxidation and sweeps away the sulfur dioxide to prevent sulfation. Sulfur content of the calcine is ca 0.05% sulfide and 0.35% sulfate. The dust problem is reduced by carrying over only 20% of the calcine to the boiler. A relatively long retention and high temperature (up to 1060°C) tend to eliminate chlorides, fluorides, mercury, and selenium. Ores containing low melting materials such as silica and magnesia do not create sticking problems. A disadvantage is the need for considerable grinding before leaching.

The New Jersey Zinc Company patented a fluidized-pellet roaster which was installed in several zinc plants. Called a fluid-column roaster, it resembles

a shaft furnace and can handle 370 t of concentrate per day. This roaster can be operated at 1080–1100°C to eliminate 90% of the cadmium and 92% of the lead. The fluid-column roaster has the same advantages as the Overpelt roaster; the pelletizing cost is a disadvantage for both systems.

Horsehead Zinc, Monaca, Pa., uses a fluid-bed roaster to finish the roasting at 950°C of material that has been deleaded in a modified multiple-hearth furnace operated with insufficient oxidation (37). First, sulfur is reduced from 31 to 22% and lead from 0.5 to 0.013%. Somewhat aggregated, the product is hammer-milled before final roasting. One-half of the calcined product is bed overflow and special hot cyclones before the boiler remove the other half; total sulfur is ~1.5%. Boiler and precipitator dusts are higher in sulfur, lead, etc., and are separated.

Sintering. Sintering before further pyrometallurgical smelting completes the roast, eliminates volatile material, and aggregates fine calcine. Aggregates need considerable strength and porosity in vertical retorts, electrothermic furnaces, and the Imperial Smelting process (ISF). Sintering practice can be classified as follows (25): on low sulfur calcine with carbonaceous fuel in one or two stages; on unroasted concentrates with high sinter recycle; and on 7–9% sulfur calcine without fuel. Zinciferous material is mixed with carbonaceous fuel, if necessary, and water. The mix is pelletized, or partly so, and fed onto a traveling endless grate. After ignition, air is drawn through the bed to burn the carbon and zinc sulfide.

Sintering machines, usually of the Dwight-Lloyd downdraft type, are used. In downdraft operations, metallic impurities are usually not eliminated in one pass because they tend to condense in the bottom portion of the bed. For this reason, the product is sliced from the top of the 10–20-cm bed and the bottom fraction (20–40%) recycled or used where the impurity can be tolerated. Chloride may be added to improve the transfer of cadmium and lead from the bed into the windbox and downstream dust and fume-collection system. Since the electrothermic zinc process requires very strong pellets, double sintering is practiced with silica flux added to the second stage. Heat is not recovered from downdraft sintering operations because of high gas volumes, moisture in the charge, and large sinter recycle loads, and a considerable energy debit is incurred. In addition, it is expensive to scrub the dilute sulfur dioxide in the off-gases.

Updraft sintering is used on unroasted concentrates and the off-gases are built to a high enough sulfur dioxide content (5–6.5%) to allow sulfuric acid production. This is accomplished by preventing gas leakage around the bed with grease-sealed slide rails and by gas recirculation. In order to avoid excessive bed temperatures and maintain porosity, sinter recycle (~80%) is high. Some heat is recovered to heat incoming air.

5.3. Reduction. Electrolytic Process. The electrolytic process, where zinc is deposited from an aqueous solution onto the cathode, treats complex ores that did not lend themselves to pyrometallurgical recovery. For example, some abundant ores containing combinations of lead and copper, silver, iron, and zinc could be concentrated to only 30–40% zinc, an unsuitable level for pyrometallurgy. The first successful electrolytic zinc plant was built by the Anaconda Company at Anaconda, Montana, and began production in 1915. The sulfide concentrate is oxidized to crude oxide and leached with return acid

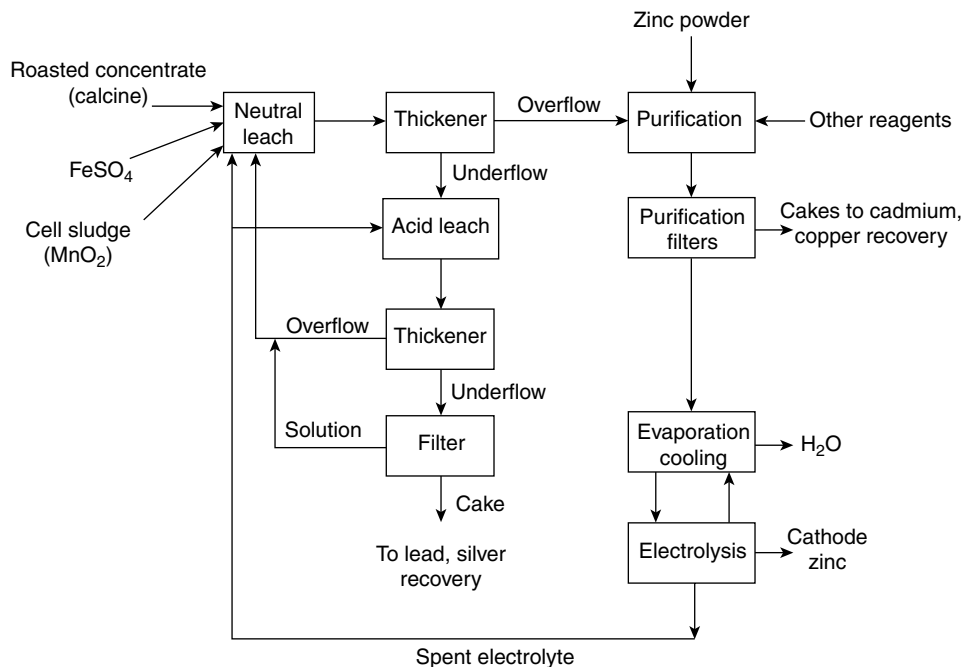


Fig. 1. Simplified flow diagram, electrolytic zinc.

from the cells. The zinc sulfate solution is purified and electrolyzed. Some plants also feed crude zinc oxide from pyrometallurgical recovery operations. At present, there are four electrolytic zinc plants in the United States with annual capacities from 50,000 to 100,000 metric tons. A simplified flow diagram is shown in Fig. 1 and detailed descriptions of plants and processes are given in the literature (38–42).

Leaching. Crude zinc oxide in the form of roasted concentrate and, at some plants, fume from slag-fuming is fed to the leach circuit where zinc is solubilized with 100–200 g/L sulfuric acid which has been returned from the cells. Grinding is integrated into the leaching step. Zinc ferrite formed in roasting is not soluble in the dilute acid and this zinc is recovered. Residues also contain lead and often silver. The pH of the solution from which the residue is separated is ~ 5.0 where hydrous iron(III), aluminum, indium, and silicon oxides are precipitated, but basic zinc sulfate is not. The hydrous oxides adsorb arsenic, antimony, germanium, and other impurities. Thus, leaching is important in purification.

Leaching is a one- or two-step procedure, batch or continuous. In one-step leaches, calcine is added to neutralize return acid until the soluble zinc is in solution and the pH is high enough to precipitate iron(III) and other impurity hydroxides. The final pH adjustment may be made with lime or limestone instead of calcine to decrease zinc loss to the residue. Although the one-step procedure is simple and requires less capital equipment than the two-step, it must be carefully controlled to ensure zinc dissolution and avoid precipitation of basic zinc sulfate above pH 5.5. Residues containing 15–20% zinc (primarily ferrite) are

sent for pyrometallurgical recovery. In the two-step procedure, more impurities are removed. New zinc plants use various modifications of this procedure because it includes recovery of the ferritic zinc. The first leach of the two-step procedure is called the neutral leach. Excess calcine is added to about one-half of the return acid plus acidic solution from the second leach step to precipitate iron and other impurities and ensure a pH (5.0–5.2) high enough for proper flocculation of the residue. The leachate is sent to the purification section and the residue, containing ~50–75% of the available zinc, is leached with acid to dissolve the remaining available zinc. The final acid contains 3–5 g zinc/L and, although some of the impurities remain in the solution returning to neutral leach, most remains with the residue. Depending on the ore, the residue may also contain lead, copper, silver, and gold. In many plants, the hot acid leach (95°C) dissolves zinc ferrites and other values that otherwise would result in the loss of up to 15% of the zinc and higher proportions of cadmium and copper.

The leaching is 50–60°C without external heating. The cone-bottom tanks are equipped with a pipe from just above the solution level to near the bottom through which air is blown forming bubbles that lower the density of the slurry. These leach tanks, called Pachucas, are fairly efficient and are still popular although many plants employ mechanical agitators. Most plants use 3–5 tanks in series with acid and calcine being fed to the first and, in some cases, downstream from the first tank as well.

Recovery of Zinc from Leach Residue. The residues from dilute acid leaching contain zinc ferrite, entrained zinc sulfate, undissolved zinc oxide, and other values, such as lead, copper, silver and gold. Although hot acid leaching improves copper and zinc recovery, the process was not widely used in the past because of the difficulty of separating iron which forms a gelatinous precipitate. Usually the residue was treated pyrometallurgically and often still is.

In addition, three commercially successful methods have been developed in which iron(III) precipitates are formed that filter and wash well, and that increase the recovery of zinc by 10–15%.

The jarosite process separates iron(III) from zinc in acid solution by precipitation of $MFe_3(OH)_6(SO_4)_2$, where M is an alkali metal (usually sodium) or ammonium (see Fig. 2) (43,44). Other monovalent and hydronium ions also form jarosites that are found in the precipitate to some degree. Properly seeded, the relatively coarse jarosite can be separated from the zinc-bearing solution efficiently. The reaction is usually carried out at 95°C by adding ammonia or sodium hydroxide after the pH has been adjusted with calcine and the iron oxidized. The neutral leach residue is leached in hot acid (spent + makeup) with final acidity >20 g/L and essentially all the zinc, including ferrite, is solubilized. Ammonium jarosite is then precipitated in the presence of the residue or after separating it. If the residue contains appreciable lead or silver, they are first separated to avoid loss to the jarosite waste solids. Minimum use of calcine in jarosite neutralization is required for maximum recovery of lead and silver as well as zinc and other metals.

In a modification, the conversion process, the jarosite residue is hydrothermally decomposed to hematite by autoclaving at 220–250°C. This solubilizes zinc and other metal values and the hematite has a potential for iron recovery. Hematite stockpiles are less of a problem than jarosite because hematite is denser and holds up less of the soluble metals.

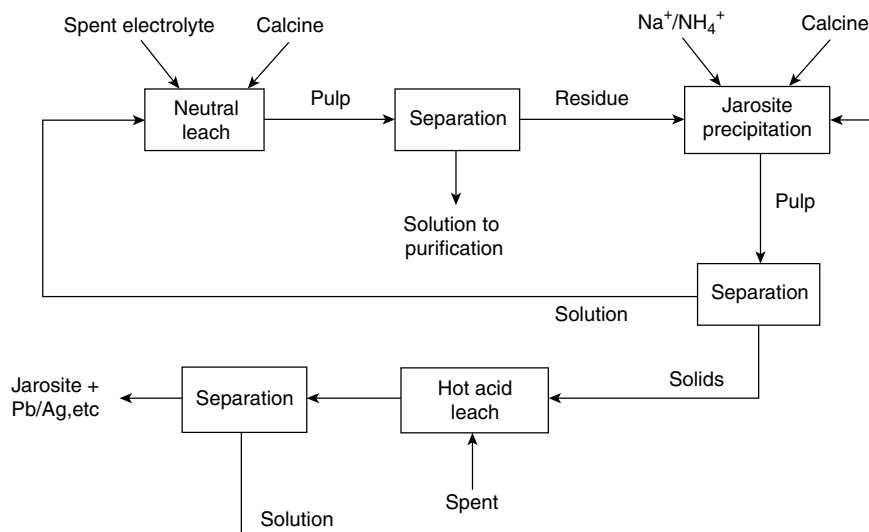


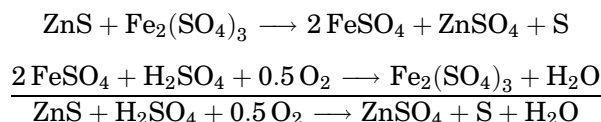
Fig. 2. Flow sheet for modified jarosite precipitation process.

The jarosite process controls both alkali metals and sulfate in the zinc-plant circuit and consumes little neutralizing agent. It is used in 16 plants worldwide, which account for ~25% of the noncommunist world's primary zinc output.

The goethite process precipitates crystalline $\alpha\text{FeO}\cdot\text{OH}$ (goethite) as well as $\text{FeO}\cdot\text{OH}$, Fe_2O_3 , and amorphous phases. The reaction is carried out at 90°C and pH 3.0, for 4–6 h in either batch or continuous fashion, and the iron(III) ion must be kept $<1\text{ g/L}$. Both jarosite and goethite solids are usually lagooned.

The hematite process is used at the Iijima plant of the Akita Zinc Co. in Japan, where it started in 1972, and at Ruhr-Zink, Datteln, FRG. In the Iijima process, neutral leach residue is leached with hot acid and the iron(III) in the leachate is reduced with sulfur dioxide at $\sim 100^\circ\text{C}$. Copper is precipitated with hydrogen sulfide although it is not essential to the process. Ruhr-Zink reduces with concentrate, zinc sulfide, giving elemental sulfur as product. Sulfur and unreacted zinc concentrate are coagulated at elevated pressure and temperature and separated by classification from finer lead–silver residue. The solution is neutralized to pH 4.5 with limestone to yield gypsum, which is filtered and sold. This leaves iron(II) sulfate solution from which Fe_2O_3 is precipitated by oxidizing at $\sim 190^\circ\text{C}$ under an oxygen pressure of 8.4 kPa (63 mmHg). The hematite product is denser than jarosite or goethite; it can be sold to steel and cement plants.

Direct Leaching of Concentrates. Sherritt Gordon Mines, Ltd., has adapted the process first used on nickel sulfide ores to zinc sulfide oxidation with air in aqueous slurry under pressure (45,46). The concentrates are leached directly with return acid from the cells and the sulfide is converted to free sulfur:



Thus, roasting is avoided. The process, especially amenable to high iron and copper concentrates, has been installed by Cominco, Ltd. (47) at Trail, B.C., Canada, and at the plant at Timmins, Ontario.

Purification. Purification of the electrolyte is extremely important since the presence of impurities, even in trace amounts, can seriously impede or halt production (48,49). Impurities may lower the hydrogen overvoltage causing the electrical energy to be consumed in depositing hydrogen instead of zinc. The reversible deposition potential of hydrogen from acid onto platinum is 1.70 V, but on zinc, because of overvoltage, it is 2.4 V. The standard potential needed for zinc reduction is 2.35 V (48). Therefore, if the hydrogen potential is lowered by a mere 0.05 V, it is deposited strongly in competition with zinc. Very low impurity levels are usually very harmful and some exhibit synergism. For example, although cobalt is tolerated in some cells at up to 10 mg/L, it increases the damage caused by germanium. Therefore, it is difficult to assess the true effect of various impurities especially since temperature, current density, and electrolyte concentration are also factors. The effects of various impurities are given in Table 6.

Purification actually starts with the precipitation of the hydrous oxides of iron, alumina, silica, and tin, which carry along arsenic, antimony, and, to some extent, germanium. Lead and silver sulfates coprecipitate but lead is reintroduced into the electrolyte by anode corrosion, as is aluminum from the cathodes; and copper by bus-bar corrosion.

Purification is primarily based upon displacement from solution, ie, so-called cementation with metallic zinc of the metals below zinc on the electromotive series. For this purpose, zinc is melted and atomized with an air jet to so-called zinc dust, which is screened into fractions in the range 70–300 μm (~ 50 –200 mesh) for use. Zinc is added in large excess over stoichiometric and $\sim 5\%$ of the cathode zinc is recycled for this purpose. Cobalt is removed in some plants by precipitation with -nitroso-naphthol. In one plant, dimethylglyoxime is used to insolubilize nickel. Most importantly, magnesium, alkali metals, chloride, and fluoride are not removed by iron precipitation or cementation, but by stripping the zinc from a portion of the electrolyte and discarding the solution. The plant solutions are saturated with calcium sulfate and incoming calcium is precipitated as gypsum at relatively cool points, eg, the cooling towers and coils. Gypsum is an important outlet for sulfate that enters with the calcine in small amounts.

Purification is highly specific for any given plant and ore composition. In general, the zinc-dust particle size, pH, temperature, agitation, and presence of additives (eg, copper, arsenic, and antimony) are important in determining the reaction rate. Both batch and continuous procedures are employed. Final polishing stages using minimal zinc are sometimes added. The three most popular purification flow sheets are described in Table 7 (50), but many variations are practiced, eg, new three-stage procedures (51,52).

Copper sulfate, in small amounts, activates the zinc dust by forming zinc-copper couples. Arsenic(III) and antimony(III) oxides are used to remove cobalt and nickel; they activate the zinc and form intermetallic compounds such as CoAs (52). Antimony is less toxic than arsenic and its hydride, stibine, is less stable than arsine and does not form as readily. Hydrogen, formed in the purification

Table 6. Effect of Impurities in Zinc Electrowinning

Impurity	Reported range—11 plants	Class ^a	Effect			
			Current efficiency	Resolution	Deposit	Other
germanium	0.005–0.2 mg/L	4	lowers	high	spongy	worse with cobalt
tellurium	<0.001 mg/L ^b	4	lowers	high	uneven	worse with cobalt
selenium	<0.002 mg/L ^b	4	lowers	high	uneven	
arsenic	0.003–0.02 mg/L	4	lowers	high	corrugated	worse with cobalt
antimony	0.01–0.03 mg/L	4	lowers	high	beady poor adhesion	worse with cobalt or germanium
copper	0.05–0.2 mg/L	4	lowers	yes		
nickel	<0.01–0.5 mg/L	3	lowers	mild	holes	
cobalt	0.03–2.0 mg/L	3	lowers	mild	holes	reduces lead deposition
tin	<0.02 mg/L	3	lowers	yes	filmy	
iron	0.2–25 mg/L	3	lowers			may reduce anode corrosion
cadmium	0.01–5 mg/L	2				deposits with zinc
lead	1 mg/L	2				deposits with zinc
thallium	0.5–5 mg/L					increases lead deposition, deposits
aluminum	10 mg/L	1				increases electrolyte resistivity
magnesium	6.5–12 g/L	1				increases electrolyte resistivity
manganese	3–3.5 g/L	1				oxide forms on anode, lowers corrosion, may insulate anode
chloride	20–100 mg/L					corrodes lead anodes
fluoride	2 mg/L					corrodes electrodes, causes sticking of zinc to cathode

^aClass 1. Higher reduction potential than zinc. Will not deposit on cathode, but will affect conductivity. Class 2. Lower reduction potential than zinc. Hydrogen overvoltage above 0.65 V. Deposits with zinc, but does not affect zinc deposition. Class 3. Reduction potential between zinc and hydrogen. May deposit and redissolve, affecting current efficiency. Causes local lowering of hydrogen overvoltage, making pits, holes, etc. Class 4. Reduction potential below hydrogen. Hydrogen overvoltage <0.65 V. Deposits and causes hydrogen evolution. Tends to form hydrides.

^bOne plant reporting.

Table 7. Purification of Zinc Liquor

Stage	Conventional arsenic ^a	Conventional antimony ^a	Reverse antimony ^b
stage 1			
remove	Co, Cu, Ni, As, Sb	Co, Cu, Ni, Cd	Cu, Cd, Tl
reagent	coarse Zn, CuSO ₄ , ^c As ₂ O ₃	coarse Zn, Sb ^d	Zn
temperature, °C	90	65–75	ambient
pH	4.0		
stage 2			
remove	Cd, Tl	Co, Cu, Ni, Cd	Co, Ge, Ni
reagent	Zn	fine Zn	Zn, Sb
temperature, °C	70–80	ambient	90
pH	3.0		

^aTo remove Co and Ni in stage 1 (hot).

^bReverse antimony: stage 2, Sb (hot) for Co, Ni removal.

^cCuSO₄ added if Cu is <400 mg/L.

^d-Nitroso-naphthol may be substituted for Sb to precipitate Co.

tanks, may give these hydrides and venting and surveillance is mandatory. The reverse antimony procedure gives a good separation of cadmium and cobalt.

Aeration must be avoided since it can oxidize and resolubilize the cemented (precipitated) impurities. Filter presses are used after each step and the cakes are leached to recover various values. For example, cadmium is dissolved, reelemented with zinc, and recovered on site either electrolytically or by distillation. A copper residue of 25–60% copper is sold for recovery elsewhere. The other impurities cannot be recovered economically with the exception of cobalt in some plants.

Electrolysis. The net electrochemical reaction is $\text{ZnSO}_4 + \text{H}_2\text{O} \rightarrow \text{Zn} + \text{H}_2\text{SO}_4 + 0.5 \text{O}_2$. Electrolysis is carried out in cells with 17–44 aluminum cathodes and 18–45 lead anodes per cell (33,53). Cell tanks are usually concrete lined with lead, rubber, or plastic. Anodes and cathodes in a given cell are connected in parallel with an imposed voltage of 3.3–3.8 V, which is higher than the standard 2.35 V because of the resistance of the electrolyte, gaseous and solid films on the electrodes, and contact resistance. Energy consumed is 3.3 kW·h/kg zinc at slightly >50% efficiency. Cells are arranged in groups connected in series with direct current (dc) supplied by rectifiers that are controlled by load-optimizing equipment in many plants. Thus, the power consumption varies, lower during peak demand period and higher during off-hours.

Increasing the current density increases the zinc-output rate per cell. Electrolytic plants were formerly classified as either low current density (200–450 A/m²)—low acid (<6%) or high current density (1000 A/m²)—high acid (22–28%). The ratio of zinc to acid in solution must be kept high enough to avoid resolution of cathode zinc, and therefore high acid plants operate at higher zinc levels. At higher current density, more heat must be removed and solution purity is more critical, but the return acid can more readily dissolve zinc ferrite formed in roasting. The choice of current density to use is therefore determined by many factors. Modern plants have current densities of 300–600 A/m² and achieve efficiencies of slightly >90% in good operation (see Table 8). Glue (≤100 mg/L) improves the smoothness of the cathode deposit and moderates the effect of impurities (55).

Table 8. Cellhouse Operating Parameters^a

Parameters	Big River Zinc, Illinois	Pasminco Ltd., Tasmania	Canadian Electrolytic Zinc Valleyfield, Quebec	UMICORE Balen, Belgium	PASMINCO Clarksville, Tennessee	Mitsubishi Akita, Japan	Mitsui Hikoshima, Japan
electrolyte							
Zn, g/L	55	46	70	50	90 (65) ^b	47	not available
H ₂ SO ₄ , g/L	200	100	200	190	128 (175) ^b	115	not available
temperature, °C		35	35	30	32	36	36
cell							
arrangement		row ^c	row	row	row	row	row
cathodes/cell	cascade	48	36	44	49	39	33
cathode area, m ²	0.65	0.65	1.1	2.6	2.6	1.6	1.6
current density, A/m ²	807	540	500–700	300–400	375	370–430	300–600
voltage	3.8	3.5	3.5	3.3–3.5	3.3	3.55	
liner	lead	lead	lead	PVC ^d	PVC ^d	rubber	rubber
deposition, h	24	72	24				
stripping							
type	auto	auto	auto ^d	auto	auto	auto	auto
removal	knives	knives	knives	knives	knives	hinged rubber edge-knives	high frequency shake
cycle, h				48	48	48	32–48

^aOlder plants are described in Ref. 54.^bSecondary cells.^cNew section.^dPoly (vinyl chloride) = PVC.

The purified zinc solution is fed to the electrolyte recirculating stream at a rate that holds the composition of the electrolyte constant, commonly ranging from 100 to 200 g H_2SO_4 and 45–70 g Zn/L. Continuous monitoring of the density and conductivity of the spent acid aids in control. This is important since the range of acidity is narrow for maximum current efficiency at any given current density.

The cells are fed individually, but cascading is practiced in some older plants. In this system, electrolyte overflows from one cell to the next in a series of 3–9 cells. More commonly, cells are placed in rows, with each cell overflowing into a common spent-acid launder.

Cooling by means of evaporative cooling towers is required to maintain a constant temperature of 30–40°C. At higher temperatures, the deposit is rougher, impurity effects are more pronounced, lead codeposition is favored, and the manganese dioxide formed at the anode increases and tends to adhere rather than fall to the bottom of the cell.

Oxygen evolved from the anodes as well as some hydrogen from the cathodes produces a mist that is trapped by a froth maintained by adding cresylic acid, sodium silicate, and gum arabic, or glue plus cresol. Alkaline-earth carbonates prevent lead contamination of the cathode zinc. Most of the lead is deposited in the cell sludge as insoluble carbonate sulfate.

Cells and anodes are cleaned on a cycle of 40–90 days when the sludge, mostly manganese dioxide, is pumped out. The manganese dioxide coating on the anodes is removed with water jets and the anodes are mechanically straightened. Aluminum cathodes are welded to aluminum header bars that have copper contact points welded or cast on. The aluminum is polished at a frequency depending on the corrosiveness of the electrolyte. Cathodes are often anodized to minimize corrosion by brief contact with the “live” anodes upon reentering the cell after stripping. Chlorides and fluorides are corrosive and make the zinc adhere to the cathode. This is especially critical in mechanized stripping operations that are rapidly replacing the manual method. Antimony chemicals are added in some plants (≤ 0.08 mg Sb/L) to combat sticking. Manual stripping of the deposit from the cathodes has always been an expensive and onerous task. Several plants adapted automatic mechanical strippers to existing cellhouses and, in 1969, Union Minere started a fully automated cellhouse at Balen, Belgium, featuring jumbo cathodes of large area (2.6 m²).

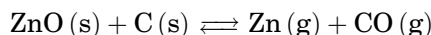
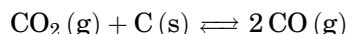
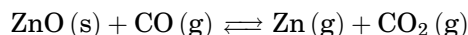
Melting, Casting, Zinc Dust. Cathode zinc is melted, usually by induction heating, and distributed by pump to a casting machine that produces 26-kg slabs of special high grade zinc. Larger castings of 1090 and 450 kg, eg, are made in preheated molds. Some of the zinc may be pumped to an alloying furnace for the addition of metals, such as lead, aluminum, and copper. These alloys are cast into slabs, jumbo blocks, and special shapes.

Some of the melted zinc is fed to the zinc-dust unit where the molten zinc may be dropped from a crucible through a small orifice (2.5 mm) to be atomized in a blast of air. Solidified droplets are collected in a chamber and screened to the proper size for purification and cadmium plant cementation. Frequently, coarse (+70–200 μm) and fine (–70 μm) fractions are required.

Ammonium chloride is used as a flux in the melting furnace because the large surface of the cathodes favors the formation of dross, ie, oxide-coated

globules of zinc. The dross is separated by liquation or air-swept milling into metal and oxide fractions. In the latter, the oxide fraction is swept out of the mill and can be returned to roasting for the elimination of chloride. Metallic zinc is recycled. Overall melting efficiency is 96–98%.

Pyrometallurgical Processes. Zinc pyrometallurgy is based upon reduction of zinc oxide (56).



The lowest temperature for the reaction is 857°C, but 1100–1300°C is required for acceptable rates. In this range, the two component reactions proceed at about the same rate and the reduction is diffusion controlled (57). Both reactions are reversible and the overall reaction is endothermic, requiring $\sim 5.5 \text{ GJ/t Zn}$ ($1.2 \times 10^9 \text{ cal/short ton Zn}$) at 1200 K.

Carbon monoxide and carbon dioxide oxidize zinc vapor <1100–1300°C, although only the carbon dioxide reaction is significant. Rapid condensation of the zinc vapor avoids the formation of zinc oxide-coated droplets, so-called blue powder.

At first, batchwise horizontal retorts were used for smelting, and later continuous vertical retorts, both externally fired. Continuous, internally heated furnaces, such as the electrothermic furnace followed, and the last important development was the Imperial Smelting blast furnace.

Imperial Smelting Furnace. In the ISF process, zinc vapor is produced in a blast furnace along with lead. Although air is introduced to provide heat through the burning of coke, the atmosphere in the upper portion of the furnace is not oxidizing despite the carbon dioxide content ($\text{CO}_2/\text{CO} = 10\%/25\%$) because of the high temperature, 1000–1050°C. To prevent reaction of carbon dioxide with zinc vapor, the gases leaving the furnace are rapidly cooled to 550–600°C in splash condensers (see Fig. 3).

The Imperial Smelting Corporation, Ltd., brought its blast furnace on-stream at Avonmouth, UK, in 1952 (58), and in 2003 there were 12 operating ISF plants around the world ranging in capacity from 30,000 to 105,000 metric tons/year. There are none in the United States, Mexico, or Canada since the Brunswick Mining & Smelting Corporation plant at Belledune, N.B., Canada, was converted to straight lead in 1972. The ISF can handle complex zinc–lead–copper ores, zinc-containing dust from steelmaking, drosses, leach plant residues, etc, in a large, economical unit. The ISF is more energy efficient (37.9 GJ/t or $32.6 \times 10^6 \text{ Btu/short ton Prime Western Zinc}$) than either the vertical retort (60.2 GJ/t or $51.8 \times 10^6 \text{ Btu/short ton}$) or the electrothermic (72.2 GJ/t or $62.1 \times 10^6 \text{ Btu/short ton}$) processes (59). In fact, the figures favor the ISF over electrolytic (49.8 GJ/t or 42.9 Btu/short ton) for Prime Western and 44.8 versus 50.1 GJ/t (38.6 vs. $43.1 \times 10^6 \text{ Btu/t}$) for special high grade (60). The electrolytic process, however, uses lower cost fuel in some locations and has other cost advantages including labor and environmental.

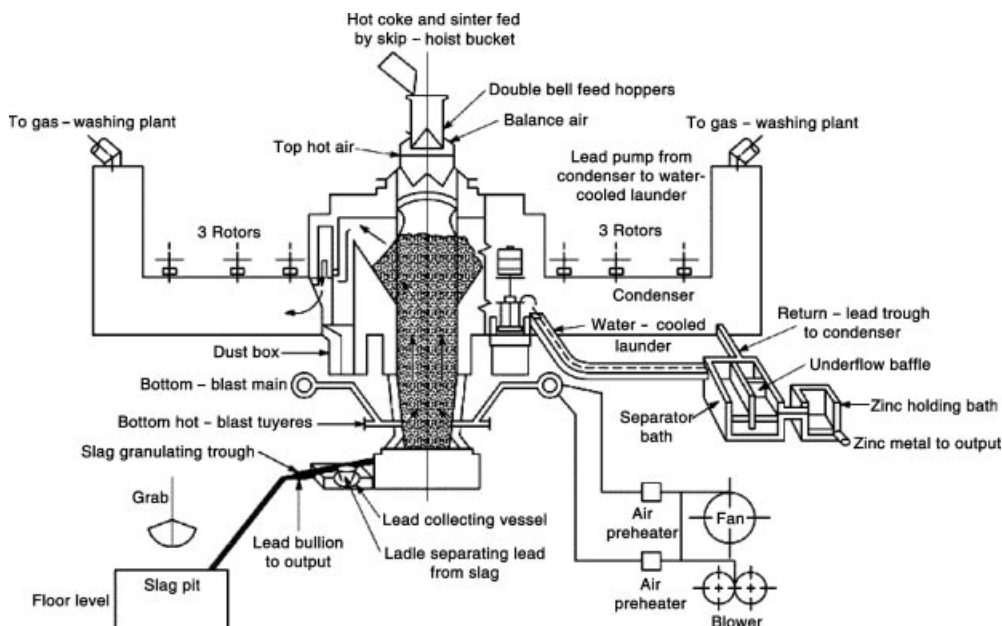


Fig. 3. Imperial Smelting furnace.

Feeds have lead/zinc ratios from 0.45 to 0.82 (61). The feed mix, primarily sulfide concentrate, is updraft-sintered and oxidized with the off-gases passing to an acid plant. Most of the cadmium is eliminated in the sintering step and the lead oxide, if >7% lead, acts as a flux to produce the hard sinter required for the blast furnace (61). Only a small portion of the sintering heat is recovered compared to the waste heat recovered in fluid-bed roasting. Hot, briquetted, roasted concentrate, or oxidized ore is an alternative to sintering, especially where lead is low. This approach is being used to supplement sintered feed up to 25%. Successful trials of 100% briquetted feed have been made, opening the possibility of using the ISF for zinc alone.

Sinter and metallurgical coke are preheated to 400 and 800°C, respectively, and fed into the top of the blast furnace through a double-bell hopper. Preheated air (800–1000°C) is blown in through tuyeres near the bottom providing heat and carbon monoxide by oxidation of the coke. Lead, silver, and copper are deposited in the molten lead bullion tapped from the furnace bottom. Slag floats on top of the bullion and is tapped periodically. Zinc vapor exiting the top is heated to 1000°C by combusting the off-gas with injected air and is rapidly condensed in a spray of molten lead after which the molten metals flow to a cooler where a zinc-rich layer overflows and the high lead bottom recirculates to the splash condenser. Zinc recoveries range from 92 to 95% and, with lead at 1.1–1.3%, the zinc is in the Prime Western class.

Since a large amount of heat must be absorbed at the condenser, the lead recirculation rate is very high, 300–500 t/h per condenser or 400 t lead per ton zinc. Heat lost to the cooling water is not recovered, but heat is recovered from the condenser off-gases (LCV or low calorific value gas) at 450°C in most plants to

Table 9. Imperial Smelting Furnace Performance^a

Characteristic	Value
production, ^b t/day	
Zn	256
Pb	128
input ratio	
Pb:Zn	0.5
C:Zn	0.75
Zn in slag, %	7.0
slag:slab Zn	0.65
recovery, %	
Zn	94.5
Pb	95.0
carbon burned per metric ton slab Zn	0.82

^aRef. 61.^bFull blast.

preheat air, coke, etc. Consideration is being given to using a waste-heat boiler at this point. The Hachinohe smelter in Japan has reported on heat recovery from LCV gas and other energy savings (62).

Grades purer than the Prime Western product have been made by vacuum dezincing the liquid alloy to recover 99.9% zinc at 0.02% lead. Distillation (New Jersey Zinc process) produces a purer product at a considerable cost in energy.

The ISFs range in shaft area from 15.3 to 27.1 m² and produce from 112 to 334 t/day. The standard furnace is 17.2 m² and its typical performance is given in Table 9 (61).

Efficiency is improved and cost is lowered by the following changes:

Hot (500–700°C) binderless briquetting of oxidized zinc and lead feed materials to replace sintering (see SIZE ENLARGEMENT).

Changes in furnace design. More uniform charge distribution, new furnace shapes, and tuyere design.

Drying of the air blast lowers coke usage 3% for each 1% of water vapor removed.

Heat recovery from furnace off-gas (LCV gas) normally used to preheat coke and blast air; LCV gas has also been burned to heat melting baths and generate steam and power.

Vertical Retort. The vertical retort process was developed by The New Jersey Zinc Company (63). Production started in 1929 at Palmerton, Pennsylvania. A charge of 25% bituminous coal, 10% anthracite, 10% recirculated fines, and 55% sinter is mixed with suitable binders and densified in a chaser mill. The mix is briquetted and coked autogenously, ie, the volatile from the coking process burn in the bed of briquettes to supply the needed heat. Briquettes leave the coker at ~700°C and are transferred to the top of the retort where they are charged on a periodic cycle. Radiant heat from the walls drives the reduction as the briquettes descend. The loaf-shaped briquettes, strong enough to withstand breakage, are extracted from the bottom through a water seal. Carbon monoxide forces the zinc vapor up the column; ~95% of the metal is condensed and the balance scrubbed out.

The Palmerton, Pennsylvania, plant had 43 retorts with an output of ~ 8 t/day per retort. Recovery was $\sim 94\%$ when the plant was shut down in 1980. The zinc contained $\sim 0.3\%$ lead, 0.10% cadmium, and 0.01% iron plus minor impurities. Lead and aluminum are added to produce galvanizer's zinc. Vertical retorts were operating in 2003 in Chinese zinc smelters in Changsha, Huludao and Shui Koushan.

Zinc of 99.995% purity is produced in fractional-distillation columns that were developed along with the vertical retorts. Refining is a two-stage procedure in which higher boiling lead and iron are separated in the first column, whereas lower boiling cadmium is distilled in a second column (64).

Electrothermic Process. Electric-arc furnaces with molten iron-slag baths have never been successful despite many attempts (65). However, a process developed by the St. Joseph Lead Company (now Doe Run Company), based upon resistance heating, was employed in four plants in 1981 (37). There is relatively little dusting and zinc condensation is efficient.

Sintering is done in two stages. The second stage, with sand, produces a high purity, hard sinter that is required for the oxide and high grade zinc furnaces. Single-stage sinter is fed to the Prime Western and intermediate-grade circuits. Both sinters are sized to 9–25 mm. Coke is fed at $\sim 300\%$. Small furnaces have daily outputs of 16–25 t, large ones have outputs of 100 t. Current consumption is 1250 kW/electrode pair at 200–230 V. Vapor exits through an annular vapor ring and is led to the condenser.

The Weaton-Najarian zinc condenser was commercialized in 1936. The condenser and cooling well of the electrothermic furnace holds 48 t of molten zinc. Hot zinc-laden gases bubble through the zinc in the condenser and cause rapid circulation through the cooling well, which is kept at 480–500°C by water coils. The off-gases are scrubbed and burned for fuel value. Scrubber water is ponded to recover blue powder.

Horizontal Retort. In 1800, the first commercial zinc process made use of the horizontal retort. In 1980, only three such plants remain because they are not competitive in terms of labor and fuel costs. Furthermore, the dust produced presents a serious pollution problem. Nevertheless, in 1956, the tonnage of zinc produced from horizontal retorts was above that of any previous year. The only remaining operation is in Russia with a capacity of 10,000 annual MT.

Banks of Belgian horizontal cylindrical retorts are arranged in a furnace containing 500–700 retorts. Heat is applied externally by natural or producer gas. The retorts are charged with a damp mixture (35–40% zinc) of sinter, blue powder, and carbonaceous reducing agent (50%). The cycle is ~ 48 h, and 40 kg zinc is produced per retort. The zinc vapor is liquefied in a clay condenser. Metal is drawn periodically in 10-kg lots into a ladle that is skimmed to remove blue powder and impurities. Slab zinc is cast in molds directly from the ladle and the casting is skimmed. Recoveries are 88–95%, and the quality of the metal depends on the composition of the charge.

Biological Leaching. Teck Cominco's HydroZinc process allows direct extraction of zinc metal from zinc sulfide ore by bioleaching from ore heaps. This is followed by neutralization, solvent extraction, and electrowinning. The process does not require grinding of the ore.

Secondary Recovery. Zinc is recovered as metal, dust, and chemicals (including oxide) from secondary sources, mostly scrap (see also). So-called old scrap originates from die castings and engraver's plates, whereas new scrap, eg, drosses, skimmings, flue dust, clippings, and residues, originates in various processes. In 2003, secondary slab zinc was produced in the United States at three plants as well as by two primary producers. One of these, CalEnergy, is recovering zinc from geo-thermal brine at a rate of 30,000 metric tons/year. One steel mill, Nucor-Yamato, is also recovering zinc from flue dust. Zinc dust was produced at eight plants, mostly from secondary materials. Recovery practices vary greatly, but zinc products are usually made from metallic scrap by melting and distillation. Dust is made by rapid condensation of zinc vapor in oxygen-free atmospheres; the spherical particles have diameters of 1–20 μm (2).

A novel process, called Zincex, was brought on-stream in 1976 by Metalquímica del Nervion in Bilbao, Spain, where 8000 t/year is produced from pyrite cinders (66). The cinders are given a chloridizing roast and leached to produce a solution containing 20–30 g/L zinc, 18–25 g/L iron, 60–100 g/L chloride, and 120–155 g/L sulfate. Solvent extraction in two stages recovers 98% of the zinc. The first stage uses a secondary amine to extract ZnCl_4^{2-} , which is stripped with water. Di-2-ethylhexyl phosphoric acid absorbs zinc ion in the second stage, where spent electrolyte is the stripping agent. Thus, zinc is well separated from chloride, iron, and other harmful impurities.

6. Economic Aspects

Zinc consumption is broken down into slab and all-classes classifications. The latter includes zinc-containing materials made from ores and residues as well as from secondary (scrap) zinc. Consumption and production figures of slab zinc show that a substantial difference exists, which is made up of imports (see Table 10). The imports consist of ore and concentrates based on zinc content, slab zinc in the form of blocks and pigs, zinc dust by gross weight, waste and scrap on a gross weight basis, and dross and skimmings based on zinc content. In 1970, ore and concentrate imports were about equal to U.S. mine production and slab zinc imports represented 30% of U.S. production. In the late 1970s, imports of ore and concentrates decreased below U.S. production and imports of slab zinc increased to exceed U.S. production from 1976 onward. Imports of ore and concentrates in 2003 came from Peru (49%), Australia (29%), and Ireland (10%). Canada supplied $\sim 54\%$ of slab zinc and Mexico supplied $\sim 17\%$. For 2003, the figures for U.S. exports are given in Table 11.

Production processes are given in Table 12. Electrolytic processes are dominant because of lower cost and fewer environmental problems. Production of slab zinc in Tennessee commenced in 1978 when Jersey Minière Zinc Company began operation of its new 90,000 t/year electrolytic smelter at Clarksville. Today, Tennessee is the leading producer of slab zinc. The U.S. smelting capacity has declined by almost 50% since 1970. Plants closed because they were obsolete and could not meet environmental standards or obtain sufficient concentrate. Consequently, slab zinc has replaced concentrates as the principal import form.

Table 10. **U.S. Production, Consumption, and Prices of Slab Zinc, 1000 t**

Use	1970	1976	1980	1996	2003
production					
domestic ores, recoverable Zn content	484.6	439.6	343.9	600	786
slab zinc					
from domestic ores	366.5	346.4	234.4	214	155
from foreign ores	429.9	106.1	113.7	12	32
from scrap	70.0	62.2	28.8	140	166
<i>total</i>	<i>866.4</i>	<i>514.7</i>	<i>376.9</i>	<i>366</i>	<i>303</i>
secondary zinc	280	225	275	238	265
imports					
ores and concentrates (Zn content)	477.0	88.1	129.9	15	164
slab zinc	245.3	648.2	410.6	827	758
other ^a	9.9	18.4	11.5	2	2
consumption					
slab zinc	1076.8	1135.8	817.9	1210	1080
all classes	1420.6	1479.0	1153.6	1450	1340
price, Prime Western, yearly average, ¢/kg					
United States	33.778	81.607	82.529		
London (LME) ^b	29.035	71.230	76.033	4650	37.53

^aZinc dust, gross weight; waste and scrap, gross weight; dross and skimmings = zinc content.^bRef. 67.Table 11. **U.S. Zinc Exports, 2003**

Material	1000 t
ores and concentrates	841
zinc pigs and slabs	2
zinc sheet and strip	10
dross, scrap, ashes, and skimmings	35
<i>total</i>	<i>888^a</i>

^aRef. 68.Table 12. **Distribution of Zinc Production Processes**

Process	Date of commercialization	Worldwide production capacity, 2003, 1000 MT ^a
electrolytic	1915	8,972
horizontal retort	1800	10
vertical retort	1930	292
electrothermic	1936	202
Imperial Smelting (ISF)	1952	810
direct Leaching	2003	150

^aRef. 16.

Table 13. **Slab-Zinc Production in the United States by Various Reduction Methods, 1000 t^a**

Year	<i>Method of reduction</i>				
	Primary		Secondary redistilled		Grand total
	Electrolytic	Distilled	At primary smelters	At secondary smelters	
1970	356.8	439.6	59.7	10.3	866.4
1975	211.7	185.8	31.7	20.8	450.0
1977	210.5	197.9	26.4	19.5	454.3
1980	295.2	52.9	15.3	13.4	376.8
1996	170	48	98	50	366
2003	230	62	98	45	435

^aRefs. 69,70.

Electrolytic and distillation processes are used to produce primary slab zinc at smelters from ores and concentrates, whereas redistillation is used to recover zinc from secondary zinc materials at both primary and secondary smelters (see Table 13) (69,70). In 1965, nearly 60% of the primary slab zinc was manufactured by the distillation process. However, in 1975, electrolytic slab zinc became dominant and by 1996 its share increased to 78%.

In 2003, secondary production including secondary zinc production and also the portion of primary zinc smelting from scrap, was twice that of primary production, whereas in 1980 it was 89% of primary zinc production. The tonnage of secondary zinc has increased largely because of recovery of zinc from electric arc furnace dust from steel making. Zinc-containing scrap utilized in 2003 was used to produce redistributed slab zinc (67%), zinc dust (2%), zinc in chemical products (25%), and other metal products (6%).

The world production of mined zinc ore and of zinc-slab production are given in Table 14. In 1996, the 13 producing countries listed accounted for 84% of the zinc mined in the world. In many cases, ore is smelted in the country in which it is mined, but an active market in zinc concentrates exists. The most notable exceptions are Germany, France, Belgium, Italy, and the Netherlands, which produce metal from imported ore in varying degrees. Mining countries that have little or no smelting capacity are Peru, Ireland, and Sweden.

Zinc consumption is categorized in five semifabricating markets (see Table 15). Galvanizing is followed by zinc-base casting alloys and brass and bronze.

6.1. Die-Casting Alloys. Consumption of die-casting alloys increased rapidly in the 1940s because of usage in the automotive industry. U.S. zinc tonnage used in die castings reached a peak in 1965 with 578,766 metric tons. The decline in the zinc die-casting market can be attributed to reduced automotive sales and competition from aluminum, magnesium, and plastics, particularly where weight limitations and reductions are required. However, the development of thin-walled die castings and improved alloys and finishing techniques indicates that die casting will continue to consume large quantities of zinc in the transportation and appliance industries. The price of zinc relative to that of aluminum and plastics and public preference for metal parts because of

Table 14. World Mine Production^a and Slab-Zinc Production, 1000 t^b

Country	1976		1980		1996		2003	
	Mine production	Slab zinc	Mine production	Slab zinc	Mine production	Slab zinc	Mine production	Slab zinc
Australia	461.9	249.2	470.6	306.0	1016	327	1480	557
Belgium		244.4		238.0		207		244
Brazil							200	387
Canada	1145.0	472.3	1058.7	586.7	1234	716	1000	700
France		233.5		252.8		324		253
Germany		304.8		368.8		327		388
Ireland	62.8		228.8		163		250	
Italy		191.2		206.4	12	269		123
Japan	260.0	742.1	236.9	743.9	80	599	45	153
Mexico	259.2		239.3		374	223	460	310
The Netherlands		123.2		168.1		207		223
People's Republic of China	135.0	150.0	155.0	160.6	1040	1079	1650	2300
Peru	413.7		492.0		758	175	1250	202
Poland	215.0	237.0	237.2	215.0	153	166	150	160
Spain	82.3		170.4		140	361	70	530
Sweden	128.3		170.0		161		187	
United States	483.0	514.7	343.9	358.6	603	366	738	303
Kazakhstan (after 1990) ^c	1020.1	1000.0	1020.1	1088.6	305 ^d	400 ^d	395	295
other	1586.2	1327.1	1391.3	1502.4	1184	1548	1135	2752
world	6252.5	5789.5	6214.2	6195.9	7223	7294	9010	9880

^aBased on zinc content.^bRefs. 69,70.^cEstimated.^dFormer USSR countries.

Table 15. Distribution of U.S. Slab-Zinc Consumption, 1000 t^a

Use	1970	1976	1980	1996	2003
galvanizing					
sheet and strip	229.7	223.8	218.9		
wire and wire rope	28.0	24.3	20.6		
tube and pipe	58.5	44.4	34.8		
fittings (for tube and pipe)	8.6	5.9	5.3		
tanks and containers	3.6	3.0	3.8		
structural shapes	17.0	31.4	19.4		
fasteners	4.8	3.7	2.7		
pole-line hardware	9.0	4.3	3.8		
fencing, wire cloth, and netting	16.4	20.0	12.1		
other and unspecified uses	54.6	32.2	23.6		
<i>total</i>	430.2	393.0	345.0	398	264
zinc-base alloys					
die-casting alloys	411.4	380.8	202.6		
dies and rod alloys	0.8	0.9	0.2		
slush and sandcasting alloys	9.1	5.7	5.6		
<i>total</i>	421.3	387.4	208.4	142	113
brass and bronze ^b					
sheet, strip, and plate	55.9	82.7	37.6		
rod and wire	37.6	49.5	32.4		
tube	8.2	6.7	4.6		
castings and billets	4.2	3.8	1.8		
copper-base ingots	9.0	7.0	17.0		
other copper-base products	0.9	1.1	3.0		
<i>total</i>	115.8	150.8	96.4	88	88 ^c
rolled zinc	37.2	27.1	21.1		
zinc oxide	39.8	35.4	29.9		
other ^d	33.0	35.3	25.0	161	
estimated undistributed consumption			91.2		
<i>grand total</i>	1077.3	1029.0	817.0	788	506

^aRefs. 69–71.^bFor zinc in brass objects, see Copper Alloys.^cIncluded in other.^dZinc dust, light metal alloys, desilvering lead, bronze and brass powders, zinc chemicals.

their durability are important factors affecting the use of zinc. The consumption for zinc die castings is given in Table 16.

6.2. Zinc Dust. World production is given in Table 17 (70), distribution of consumption in Table 18 (2). Decline since 1998 can be attributed to a reduced demand for coatings uses in automobiles.

Table 16. Markets for Zinc Die Castings, 1000 t^a

Year	Total consumption
1974	411.7
1976	377.8
1978	377.7
1980	284.7
2003	222.0

^aRefs. 70,72.

Table 17. World Production and Imports of Zinc Dust, 1000 t

1998	2003
26.9	11.9

Table 18. Worldwide Distribution of Zinc-Dust Consumption, 2003

Use	1000 t/year	Percent
coatings	81.5	28
chemical uses	163	56
batteries	46.5	16
<i>total</i>	<i>291</i>	<i>100</i>

7. Specifications and Grades

The chemical requirements for three slab-zinc grades made from ore or other material by distillation or electrolysis are specified by ASTM as given in Table 19 (73). Zinc produced by sweating or remelting of secondary zinc is not covered. Purity ranges from 98.0 to 99.99%; the main impurities are Pb, Fe, and Cd. The impurities strongly affect the physical and chemical properties. Over the years, the intermediate grades, brass special, and selected grades of slab zinc, with purities between high grade and Prime Western, have been deleted from the specification because use requirements have changed. Nevertheless, the use determines the quality standards (74).

The ability of the zinc industry to produce special high grade zinc by zinc distillation and electrolytic processes led to the development of modern zinc die-casting alloys that represent the second largest market for zinc. Because zinc die castings contain aluminum, this extra-pure grade must be extremely low in iron, lead, cadmium, and tin in order to avoid damaging intercrystalline corrosion. Such rigorous control of composition is essential for stable zinc die castings.

In galvanizing, the largest use of slab zinc, the iron or steel is dipped in molten zinc or electroplated. For hot-dip galvanizing, where automotive-grade appearance is not important, the lower grades are satisfactory. For some appli-

Table 19. Compositions of the Commercial Grades of Zinc, %^a

Grade	Lead, maximum	Iron, maximum	Cadmium, maximum	Zinc, minimum by difference
special high grade ^b	0.003	0.003	0.003	99.990
high grade	0.03	0.02	0.02	99.90
Prime Western ^c	1.4	0.05	0.20	98.0

^aWhen specified for use in the manufacture of rolled zinc or brass, aluminum max = 0.005%.

^bTin max = 0.001%.

^cAluminum max = 0.05%.

cations, such as wire, which must withstand bending without flaking of the coating, high grade or special high grade is employed. In electrogalvanizing, zinc is obtained either from zinc anodes or by direct solution from ore and subsequent purification of the electrolyte. High grade and special high grade are used for anodes in electrogalvanizing.

To meet the specification for Prime Western, zinc is debased with lead. This may increase the cost, when the price of lead is higher than that of zinc. Generally, lead, the principal impurity in Prime Western, aids the galvanizing process by increasing the fluidity of the bath and defining spangle boundaries. The solubility of lead in molten zinc at galvanizing temperatures (425–460°C) is ~ 1 –1.5% by weight. If the lead content is higher, the lead settles at the bottom of the galvanizing kettle, protecting it from attack by molten zinc and facilitating the removal of iron–zinc alloy dross.

All grades of zinc slab are used to some degree in brasses and bronzes. In many leaded brass-mill products, the lead originates from the slab zinc; the accompanying cadmium is usually acceptable.

All grades may be used in rolled zinc alloys, although special high grade and high grade are most commonly employed. When aluminum is added to superplastic zinc alloys (Zn-22 Al), special high grade is required plus protective alloying elements to prevent intergranular corrosion caused by moist service conditions, as is the case with zinc die castings.

8. Analytical Methods

Zinc in ores at the concentrating mill is often determined polarographically and mill slurries are commonly monitored continuously for zinc by X-ray fluorescence to control addition of flotation reagent (75). Low zinc concentrations in solution are analyzed polarographically or by atomic absorption spectroscopy (AAS) with a detection limit as low as 0.01 $\mu\text{g/mL}$ (76). This method is used by most modern mills for determining other metals, eg, lead, cadmium, copper, cobalt, nickel, magnesium, and calcium. Silver and gold are fire-assayed. In concentrates, where zinc is high and great precision is required, wet methods are often used, eg, the titration with potassium ferrocyanide (77).

Zinc smelters use X-ray fluorescence spectrometry to analyze for zinc and many other metals in concentrates, calcines, residues, and trace elements precipitated from solution, eg, arsenic, antimony, selenium, tellurium, and tin. X-ray analysis is also used for qualitative and semiquantitative analysis. Electrolytic smelters rely heavily on AAS and polarography for solutions, residues, and environmental samples.

Analysis of zinc solutions at the purification stage before electrolysis is critical and several metals present in low concentrations are monitored carefully. Methods vary from plant to plant, but are highly specific and usually capable of detecting 0.1 ppm or less. Colorimetric process-control methods are used for cobalt, antimony, and germanium, turbidimetric methods for cadmium and copper. Alternatively, cadmium, cobalt, and copper are determined polarographically, arsenic and antimony by a modified Gutzeit test, and nickel with a dimethylglyoxime spot test.

Finished zinc and zinc alloys are usually analyzed for metals other than zinc by emission spectroscopy and the zinc determined by difference. ASTM method E 27 describes a technique using a dissolved sample and photographic detection. The internal standard is the zinc line at 267.0 nm. However, procedures using solid samples are generally preferred and photoelectric detection often replaces optical detection. Samples are cast and machined on the surface where the arc is struck. Up to 15 elements can be determined in a few minutes by modern automatic spectrometers. ASTM gives wet chemical methods for metals other than zinc (78).

The Committee on Medical and Biologic Effects of Environmental Pollutants of the National Research Council presents a well-referenced review of zinc sampling and analysis as they pertain to physiological media, water, air, foods, soils, and plants (79). Standard methods have not yet evolved in the clinical field, but some are recommended. Most analyses today are by AAS, which uses the 213.8-nm wavelength for zinc with reported sensitivities of 0.01–0.025 $\mu\text{g/mL}$. Electrothermal atomization (graphite furnace) lowers the detection limit by up to three orders of magnitude (76). Spectrophotometric procedures are popular, commonly employing dithizone (diphenylthiocarbazone) and zincon to develop red (535 nm) and blue (620 nm), respectively. Those methods detect zinc concentrations as low as 1 $\mu\text{g/mL}$ (79). Polarography is still employed for water samples containing 0.01–0.1 mg Zn/L, but is being replaced by AAS.

9. Health and Safety Factors: Environmental Aspects

Within recent years there have been a number of review articles regarding the release, fate, and transport of zinc in our environment. The publications have provided the insight not only to the environmental hazards of zinc, but also to the biological importance of this essential element as well (80–84).

The level of natural versus manmade emissions to the environment are of a similar magnitude. Soil erosion is the major contributor of natural emissions with zinc mining, zinc production facilities, iron and steel production, corrosion of galvanized structures, coal and fuel combustion, waste disposal and incineration, and the use of zinc fertilizers and pesticides being the principal anthropogenic contributors.

The concentrations of zinc in air, water, and soil are highly variable depending on geological considerations and the influences of point sources in the area. The natural background concentrations of total zinc range from $<0.1 - 50 \mu\text{g/L}$ in freshwater, 0.002–0.1 $\mu\text{g/L}$ in seawater, 10–300 mg/kg dry weight in soil, and up to 300 ng/m³ in air.

Zinc is an essential element and thus can exist in both the deficient or toxic state in plants and animals. Deficiency occurs in some plants when the tissue content drops <20 ppm. The normal range is 25–150 ppm. The toxic effect of zinc has been seen at 400 ppm, although plants vary widely in their tolerance.

Direct application of zinc to soil to optimize growing conditions is accomplished using commercial-type fertilizers or through the application of municipal sewage sludge. The latter is closely regulated in order to prevent metals,

including zinc, from accumulating to levels that would become phytotoxic or result in an undue exposure to humans through the ingestion of food or soil.

Like plants, marine and freshwater organisms vary significantly in their response to zinc. The range of concentration among species is relatively narrow, except for oysters, which tend to accumulate zinc to very high levels. The zinc content of most seafoods ranges from 3 to 30 ppm. Oysters contain from 100–2000 ppm.

Zinc is also an essential food element in the human diet. Too little zinc in the diet can lead to poor health, reproductive problems, and a lowered ability to resist disease. Taking too much zinc into the body through food, water, or dietary supplements can also affect health. The levels of zinc that produce adverse effects are higher than the Recommended Daily Allowances, which are 15 mg/day for men, 12 mg/day for women, 10 mg/day for children, and 5 mg/day for infants.

9.1. Hazards of Production. In most zinc mines, zinc is present as the sulfide and coexists with other minerals, especially lead, copper, and cadmium. Therefore, the escape of zinc from mines and mills is accompanied by these other often more toxic materials. Mining and concentrating, usually by flotations, does not present any unusual hazards to personnel. Atmospheric pollution is of little consequence at mine sites, but considerable effort is required to flocculate and settle fine ore particles, which would find their way into receiving waters.

Drainage from active mining areas is considerably less than from inactive mines because of the disposal methods currently employed. Prior to discharge, liquid effluents are limed and settled to precipitate metals as hydroxides. Flocculants are used to reduce the total suspended solids and, in some instances, filtration of thickener overflow is practiced.

Particulate emissions are controlled mainly through venting, baghouses, and water scrubbers. Atmospheric zinc loss is estimated at 100 g/t or zinc mines, mostly from handling dry ore and concentrate and wind erosion of tailing piles. Sulfur dioxide emissions have been reduced by installing double absorption acid plants and improved containment of dilute gases.

The most significant occupational exposures to zinc would occur during the smelting and refining of zinc ore. The standards for occupational exposure have been established at a level to prevent the onset of metal fume fever. This temporary condition is caused by excessive exposure to freshly formed fumes of zinc oxide and results in flulike symptoms of fever, chills, headache, muscle pain, nausea and vomiting.

10. Uses

10.1. Metallic Coatings. Zinc coatings on iron and steel for corrosion protection represent the largest market for zinc (see Table 16). Methods in general include hot-dip galvanizing, continuous-line galvanizing, electrogalvanizing, zinc plating, zinc spraying, and painting with zinc-bearing paints (85). The automotive industry has used increasing amounts of galvanized sheet to improve corrosion protection, and the average U.S. auto today contains 7.8 kg of zinc to protect it from rust.

10.2. Die-Casting Alloys. The principal application of zinc as a structural material is in alloys for pressure die casting (see Table 16). In 2003, markets were equally divided between automotive, builders' hardware, and all other uses. The automotive industry casting uses include handles and locks, mechanical components, electrical components, body hardware and trim, lamp and lighting fittings, instruments, and other components. The zinc die castings per average car, reflecting the need for lighter weight and thin-walled castings, dropped from ~ 22.6 kg/car in 1974 and 1975 to 13.6 kg in 1978, 12.8 kg on the 1979 models, and has averaged at 10 kg/car for the last 25 years. Builder's hardware uses include covered door and window hardware, locks and keys, furniture and cabinet hardware, hand tools and cutlery, bathroom and plumbing fittings, general hardware, marine hardware, and luggage hardware.

The three zinc alloys, designated as Nos. 3, 5, and 7, are used for the hot-chamber die-casting process. Their compositions are given in Table 20 along with a cold-chamber zinc die-casting composition, No. 16 alloy (86–88). The No. 16 alloy was developed by the International Lead Zinc Research Organization (ILZRO) and has superior creep resistance at both ambient and elevated temperatures (89). Alloys ZA-87, ZA-12, and ZA-27 described later can also be die cast. ZA-8 is growing in use as a hot-chamber die-casting alloy, whereas ZA-12 and ZA-27 are cold-chamber die cast.

The zinc alloys 3, 5, and 7 are somewhat similar in properties and can generally be used interchangeably. The No. 3 alloy has excellent retention of impact strength and dimensions; No. 5 has greater hardness, tensile strength, and more resistance to creep, but suffers some loss of impact strength when used continuously at elevated temperatures; No. 7, the most recent addition to the series, has properties similar to No. 3, but is slightly softer and more ductile. Because of its lower magnesium content, it exhibits better fluidity and castability than either 3 or 5 (91).

Aluminum is the principal alloying addition varying from 3.5 to 4.3%. The Zn–Al phase diagram is shown in Fig. 4 (92). Most die-cast and foundry alloys are Zn–Al compositions. Aluminum improves die-cast strength, reduces grain size, and decreases the solution rate of iron and steel parts to the extent that a submerged plunger-type die-casting machine can be used. The spread between 3.5 and 4.3% allows sufficient latitude for production without decreasing optimum properties. An aluminum content $< 3.5\%$ promotes hot shortness, impairs the surface finish and lowers the mechanical properties. On the high aluminum side, a loss of impact strength begins at 4.5% aluminum, and at 5% the alloy is brittle. Aluminum in zinc, in the presence of excessive amounts of certain impurities (eg, Pb, Sn), can result in intergranular corrosion in die castings exposed to moist, warm atmospheres, causing them to lose strength, crack, and sometimes even disintegrate. Specifications place limits on these harmful impurities to avoid this problem, and special high grade zinc is employed for die-casting alloys (93,94).

Copper increases tensile strength and hardness and offers some protection against elements that promote intergranular corrosion. However, copper reduces impact strength and dimensional stability owing to aging and is therefore kept at 1.25% max.

Magnesium prevents intergranular corrosion by counteracting the harmful effect of small quantities of impurities, eg, tin and lead (95). The minimum values

Table 20. Compositions of Zinc Die-Casting Alloys, wt %^a

Element	No. 3 ASTM AG40A		No. 5 ASTM AC41A		No. 7		No. 16	
	Ingot ^b	Die casting ^{c,d}	Ingot ^b	Die casting ^{c,d}	Ingot ^b	Die casting ^c	Ingot	Die casting
copper	0.10 max	0.25 max ^e	0.75–1.25	0.75–1.25	0.10 max	0.25 max ^e		1.0–1.5
aluminum	3.9–4.3	3.5–4.3	3.9–4.3	3.5–4.3	3.9–4.3	3.5–4.3		0.01–0.04
magnesium	0.03–0.06	0.03–0.08 ^f	0.03–0.06	0.03–0.08 ^f	0.010–0.020	0.005–0.020		0.02
iron, max	0.075	0.100	0.075	0.100	0.075	0.100		0.04
lead, max	0.005	0.007	0.005	0.007	0.0020	0.0030		0.005
cadmium, max	0.004	0.005	0.004	0.005	0.0020	0.0020		0.004
tin, max	0.002	0.005	0.002	0.005	0.0010	0.0010		0.003
nickel					0.005–0.020	0.005–0.020		0.15–0.25
titanium								0.10–0.20
chromium								

^aZinc is the remainder.

^bASTM B 240.

^cMay contain nickel, chromium, silicon, and manganese in amounts of 0.02, 0.02, 0.035, and 0.5%, respectively. No harmful effects have ever been noted due to the presence of these elements in these concentrations; therefore, analyses are not required for these elements.

^dASTM B 86.

^eFor most commercial applications, a copper content in the range of 0.25–0.75% does not adversely affect the serviceability of die castings and should not serve as a basis for rejection; ASTM B 240-79 (90).

^fMagnesium may be as low as 0.015% provided that the lead, cadmium, and tin do not exceed 0.003, 0.003, and 0.001%, respectively.

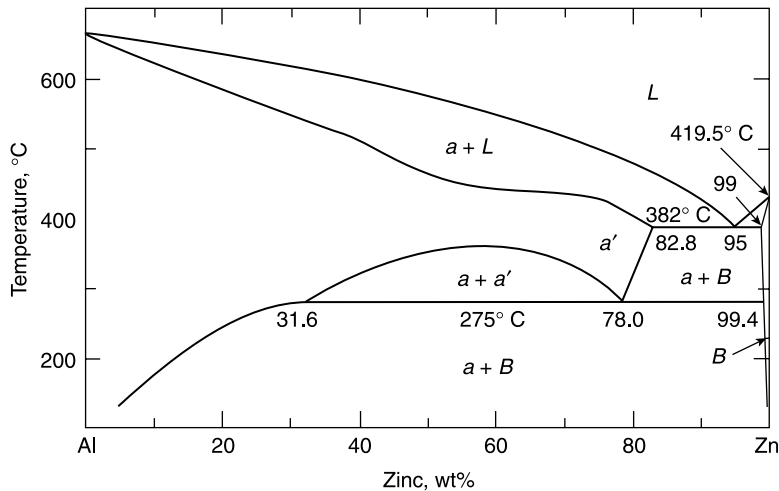


Fig. 4. Aluminum-zinc phase diagram.

for magnesium are necessary for the level of impurities allowed in the casting specification. The maximum limit for magnesium in the alloy specifications is set arbitrarily to allow some spread for commercial production. Operating close to the minimum values lessens the hot shortness and improves castability. The No. 7 alloy allows the lowest minimum magnesium content in the presence of nickel that neutralizes elements that promote intergranular corrosion. Magnesium also increases the strength and the hardness.

Maximum limits are placed on iron, lead, cadmium, and tin. The maximum limits for lead and tin are set at amounts that do not promote subsurface network corrosion at the minimum levels of magnesium allowed in the die castings. At concentrations of $\sim 0.1\%$ and higher, cadmium is detrimental to mechanical properties. Cadmium adversely affects hot shortness and castability, but the amount in special high grade zinc is too low to produce a noticeable effect. For the Nos. 3 and 5 alloys, the maximum limit is 0.004% , but for the No. 7 alloy, it is 0.002% , and special high grade zinc must be selected to meet this requirement in the preparation of this alloy. Iron has no detrimental effects on the permanence or properties, but an excess of iron may affect finishing operations, eg, machining and buffing. Zinc castings should not contain much $> 0.02\%$ iron. The ASTM limit of 0.100% iron is an arbitrary value that may be on the high side. The ASTM specification allows small quantities of nickel, chromium, silicon, and manganese which may come from aluminum used in alloying or from remelting of electroplated scrap (93).

The melting of zinc alloys for die casting entails (94) the melting down of virgin ingot; remelting of scrap from the foundry and trimming operations, and reconstitution of this melt by means of suitable additions; and the holding of quantities of molten metal at a closely controlled temperature adjacent to the die-casting machine. The furnaces are generally of the pot type, although immersion-tube and induction furnaces are also used. Heat is supplied by gas, oil, or electrical resistance. The capacity of melting furnaces is between 450

and 9000 kg; total capacity is usually five to seven times the amount of metal required per hour. The pots are made from gray or ductile cast iron. Ladles are cast iron or pressed steel. The temperature of zinc is kept at 475–500°C in the melting and alloying pots, whereas holding furnace temperatures are between 390 and 425°C, depending on the composition of the alloy being cast and part size.

Die castings are produced under pressure in permanent metal molds (96–98). Die casting with zinc-base alloys is one of the most efficient and versatile production methods that can be used for the manufacture of accurate, complex metal components. The machine used is of the so-called hot-chamber or submerged-plunger type because the alloys melt at low temperature and do not attack the injection-pump material (gray or ductile cast iron). The die-casting die or mold consists of a cover and an ejector die that meet at the parting line. Machines range in size (clamping force) from 25 to 2500 tons.

Injection pressures for hot-chamber machines are between 6.9 and 20.7 MPa (1000–3000 psi). The velocity with which the metal enters the die is controlled by the pressure and die design. The optimum may differ from each casting and in the past it has been determined primarily by trial and error. In recent years, techniques have been developed for the use of instrumentation to calibrate the shot system and die design programs are available for optimizing gate and runner systems in dies (99,100). The $P-Q^2$ technique (relationship between pressure and flow), developed by the Commonwealth Scientific and Industrial Research Organization, is utilized to characterize the rate with which the die-casting machine-shot system delivers zinc to the die. Using this information, metal flow during die filling can be controlled for castings of various sizes (101). Computer programs are available to aid the die caster in applying these rules and guidelines (102).

For casting zinc alloys, die temperatures are generally between 150 and 250°C. The lower temperatures are employed for heavy castings, higher temperatures for thin-wall castings. Hot-chamber machines can be operated rapidly with a high degree of automatic control, generally at rates of 50–500 shots/hour. Special machines greatly exceed these rates with 2000–5000 shots per hour up to 18,000/h for a zipper-casting machine. Castings may weigh from a few grams to >22.5 kg.

Zinc alloys can be cast in single-cavity, multiple-cavity, combination, or unit dies. Combination or family dies consist of a series of cavities in one die for casting two or more parts. Unit dies are separate, small dies, usually with a single cavity, which are inserted in a single master-holding die and operate several at a time in large machines.

Because temperatures for die casting are relatively low, 150–250°C, hot-worked tool steels are not generally required. For short-run dies, low alloy steels, like 4140 steel, are suitable. However, for very long runs, particularly when high dimensional accuracy is required, hot-worked tool steels, eg, H11, H12, and H13, give the longest die life. Ejector pins of nitrided H11 tool steel or of 7140 alloy steel are available as stock items for insertion in the dies. Hardenable grades of stainless steel, eg, type 440B, are often used for cores. Hot-worked tool steels, eg, H11, H12, and H13 can be used for both cores and slides. Lubricating the slides and cores with molybdenum disulfide or colloidal graphite in oil helps to ensure smooth action and to minimize wear.

The life of a casting die depends on the temperature of the metal being cast, thermal gradients within the die, and frequency of exposure to high temperature. The die life for casting zinc alloys is generally much longer than that for casting aluminum, magnesium, or copper alloys; it is not unusual for dies to last for 1 million (10^6) shots or more.

Zinc die castings may be machined, bent, swaged, or coined for finishing or for slight changes or shape (93). They can be joined by riveting, spinning, welding, and soldering in assembly operations. Corrosion resistance against atmospheric and seawater conditions is good, particularly if first treated with chromate using a weak chromic acid solution to form a passive film on the surface. Anodized coatings protect zinc against severe corrosive environments and improve wear resistance. Paint, lacquer, or enamel finishes can be applied for decorative purposes. A large number of parts are chromium plated. For such treatment, the castings are usually buffed to remove traces of parting lines and flow marks, and then plated with copper, nickel, or chromium. Other metals can also be electroplated on zinc.

During the 1970s, casting techniques for the production of thin-wall zinc die castings were developed by the ILZRO to allow the faster production of components containing less zinc at lower cost (99). Because of the resulting weight saving per part, zinc became cost- and weight-competitive with aluminum and plastic (103,104).

Castings with exceptionally thin-wall sections are produced by faster cooling rates, controlled metal injection, and a meticulous standard of die construction that is necessarily associated with automatic machine operation. Since die casting is a heat-transfer process, any reduction in the mass of metal to be chilled in each cycle allows faster operation. For the user, metal saving has not only a financial advantage, but gives a component with better strength/weight ratio since thin sections have a fine-grained structure with superior properties. Thus, castings up to ~ 3 kg can be made with walls ~ 0.75 mm thick (105,106).

Purging the die cavity with a reactive gas before metal injection eliminates gas porosity that is found in die castings because of trapped air. In the pore-free process, the air in the die cavity is displaced with oxygen or other reactive gas. When the die is charged with the molten zinc alloy, the zinc reacts with the gas to form tiny, solid particles that are dispersed throughout the pore-free casting. The absence of porosity in the castings results in improved mechanical properties. This process is still in the developmental stage for zinc die castings (107).

10.3. Foundry Alloys. The tonnage of slab zinc used in foundry applications is small compared with that used for die casting, 5334 t in 1979 and 1200 MT in 1996.

High Strength Alloys. Before 1967, the only zinc gravity-casting alloys of note were the slush and forming-die alloys. In that year, the first high strength zinc gravity-casting alloy, No. 12, was introduced with 11% Al. This alloy was originally marketed as a prototype alloy to be used in sand or permanent-mold casting of parts that would later be made as die castings, since many of its mechanical properties approximate those of die-cast alloy No. 3. However, much wider application of this alloy in the foundry industry has developed (108). Subsequently, two additional alloys were developed containing 8%

Table 21. Compositions of High Strength Zinc Foundry Alloys, wt %^a

Element	No. 8	No. 12 ^b	No. 27
aluminum	8.0–8.8	10.5–11.5	25–28
copper	0.8–1.3	0.5–1.25	2.0–2.5
magnesium	0.015–0.03	0.015–0.03	0.01–0.02
iron	0.10	0.075	0.10
lead	0.004	0.004	0.004
cadmium	0.003	0.003	0.003
tin	0.002	0.002	0.002
zinc	balance	balance	balance

^aSingle units indicate maximum amounts permitted.^bCovered by ASTM B 669-80 (108). A revision of this specification is under consideration to include Nos. 8 and 27.

aluminum (No. 8) and 27% aluminum (No. 27) (109); compositions are given in Table 21 (88,110,111). These alloys can also be pressure die cast.

Physical and mechanical properties are given in Table 22 (108–112). The densities reflect the effect of aluminum: the Zn-27% Al alloy is ~30% lighter than zinc, 17% lighter than the Zn-11% Al alloy, and 21% lighter than the Zn-8% Al alloy. All three alloys possess a good combination of mechanical properties. The sand-cast Zn-27% Al alloy is superior to the other two alloys with a tensile strength close to 50% higher. Ductility of the Zn-27% Al alloy is slightly higher; however, if ductility is required, the heat-treated condition should be specified. The Zn-27% Al alloy is also the most creep-resistant (89,111). Mechanical

Table 22. Properties of High Strength Zinc Foundry Alloys^a

Property	Alloy No. 12			Alloy No. 27	
	Alloy No. 8, permanent- mold cast	Sand cast	Permanent- mold cast	Sand cast ^b	Sand cast, H.T. ^c
physical					
density, g/cm ³	6.37	6.03	6.03	5.01	5.01
melting or solidification range, °C	375–404	377–432	377–432	375–487	375–487
mechanical					
tensile strength, MPa ^d	221–225	276–310	310–345	400–441	310–324
yield strength, 0.2% MPa ^d	207	207	214	365	255
elongation, %	1–2	1–3	4–7	3–6	8–11
Brinell hardness ^e	85–90	92–96	105–125	110–120	90–100

^aRefs. 108–112.^bPrimary purpose.^cHeat treated.^dTo convert MPa to psi, multiply by 145.^e500 kg for 30 s.

properties of these alloys are equal or superior to those of many brass, bronze, aluminum, and iron alloys.

The Zn–Al system permits manipulation of the mechanical properties by suitable heat treatment. The aluminum-rich alpha phase is especially suitable for solution hardening since it can be supersaturated by as much as 30 wt% zinc. Furthermore, both alpha and beta phases can be strengthened by precipitation because of decreasing solute solubility with decreasing temperature.

Alloys Nos. 8, 12, and 27 should not be prepared and stored in cast-iron crucibles since excessive iron pickup decreases fluidity. Many types of refractory crucibles can be used for molten zinc-aluminum alloys. Silicon carbide crucibles are generally recommended. However, unlike other alloys, zinc alloys can be cast in many types of molds, including sand, plaster, silicone rubber, graphite, and cast iron (108,112), as well as bronze, aluminum, and beryllium–copper molds. Silicone rubber and graphite molds offer some special advantages. Parts with reverse taper can be cast in silicone rubber molds because of their flexibility. Graphite is easy to machine, does not distort or warp, and promotes rapid solidification because of high thermal conductivity; >20,000 zinc alloy castings have been made with the same graphite mold (113). Castings made in graphite molds show superior surface finish and mechanical properties. Alloy No. 12 can be sand- and permanent-mold cast and graphite molds are particularly successful. Alloy No. 8 has excellent finishing characteristics and presents a low cost replacement for brass and bronze castings.

The gravity-casting alloys are gaining widespread acceptance for industrial structural parts; business machines, office equipment, builder's hardware, and marine applications (112–114). They have replaced cast iron, copper-based alloys, and aluminum alloys in many applications, eg, alloy No. 12 is used in bearing applications, where bushings have been tested in mine elevators, drill motors, 50-ton dump trucks, and drill-track rollers. The alloy bushings showed less wear than bronze when both were used in tandem on the same equipment. It is expected that zinc-based bearings and bushings will find wider acceptance as a substitute for bronze because of their lower cost and superior mechanical properties, particularly for low speed, high load-type service (110,115).

Because zinc-based alloys have low melting points, energy savings in the melting operation are substantial and the foundry operation is essentially free of fume. With the current trend of increasing energy costs and pollution control, cost benefits can be considerable (112).

Slush Alloys. Slush casting is limited generally to the production of hollow casting (116), eg, lamp bases, lighting fixtures, and casket hardware. In slush casting, a molten metal is poured into a split metal mold, generally made of bronze, until the mold is filled; the mold is immediately inverted and the liquid metal is allowed to run out, leaving a thin-shell casting behind, whose shape is a replication of the cavity walls. The thickness of the wall of the casting depends on the time interval between the filling and the inverting of the mold, as well as on the chemical and physical properties of the alloy and the temperature and composition of the mold. Skilled operators produce good castings with remarkable uniformity in weight.

Slush-casting alloys must be fairly low melting and freeze over a temperature range, ie, the liquidus and solidus temperatures must be significantly different to provide a slushy range.

Zinc slush-casting alloy compositions are based on the Zn–Al system. The two commonly used alloys have nominal aluminum contents of 4.75% Al and 5.5% Al, which fall on either side of the zinc–aluminum eutectic at 5% Al with an invariant melting point of 382°C (see Fig. 4). Special high grade zinc is employed to control impurity levels in order to avoid corrosion problems. The lower aluminum alloys with 0.25% Cu produces castings with improved mechanical properties and longer service life, because copper affords protection against corrosion. Slush casting with copper-containing alloy, however, is more difficult and yields castings with thicker walls than the straight binary Zn–5.5% Al alloy.

The cast zinc–aluminum–copper slush alloy, after aging for 10 years indoors, shows a tensile strength of 238 MPa (34,500 psi) with Charpy impact strengths of 1.4–4.1 J (1–3 ft·lbf) (85).

Forming-Die Alloys. The tonnage of slab zinc used in this application is small. The use of zinc alloy dies started in the aircraft industry during World War II (117). Zinc-based alloys cast in sand and plaster molds continue to be used for short-run dies for steel and aluminum stampings in the automotive and aircraft industries (118). Considerable cost savings are realized with these low melting zinc-based alloys that are easy to polish, machine, weld, and remelt.

The common composition is 4% Al and 3% Cu, with or without a small amount of magnesium. Other elements, eg, Ni or Ti, increase die life (119). The base alloy has tensile strengths of 210–280 MPa (30,450–40,600 psi) and Charpy impact strengths of ~20–27 J (15–20 ft·lbf) (88).

10.4. Rolled Zinc. Rolled-zinc products constitute ~2–3% of slab zinc consumed in the United States over the past 10 years. The U.S. production has declined by ~50% since 1965 (70) and in 2003 only one company producing rolling zinc products was left.

The ASTM B 69-66 (1979) gives typical compositions of rolled zinc for informational purposes and general guidance and not for specification purposes (120). The maximum solid solubilities of other metals in zinc are always small, 0.5–1% for manganese and aluminum; ~2–3% for cadmium, palladium, and copper; ~8% for silver; and 10–15% for gold; solubilities at room temperature are lower. Only fractional percentages, or minute amounts, of other metals enter the structure of the zinc crystal, and only copper, cadmium, and aluminum are added to modern zinc rolling alloys. The commercial grades of rolled zinc contain the natural impurities lead, cadmium, and iron. Rolled zinc compositions developed to meet various applications are given in Table 23 (88,121). Except for the superplastic Zn–Al, the total alloying content in the other alloys is <2%. Limits are placed on impurities like cadmium, lead, iron, tin, arsenic, bismuth, and indium, which cause hot shortness or edge cracking. Lead, tin, cadmium, and bismuth must be held at very low concentrations in aluminum containing alloys because they promote intercrystalline corrosion, which takes the form of exfoliation of the surface and general embrittlement; therefore, special high grade zinc is used in the preparation of these alloys.

The zinc is normally melted in a gas, oil, or coal-fired reverberatory furnace with a capacity up to 100 tons or in a low frequency induction furnace with a

Table 23. Rolled Zinc Alloys

Alloy	%						
	Pb	Cd	Fe	Cu	Ti	Mg	Zn
zinc, pure	0.003–0.10 max	0.003–0.007 max	0.0014–0.012 max	0.001 max			99.88–99.99
Zn–Pb–Cd–Fe	0.04–0.40	0.035–0.35	0.006–0.030 max	0.002–0.005 max			99.2
Zn–Cu	0.02–0.10 max	0.007–0.08	0.012 max	0.12–0.90			98.9
Zn–Cu–Mg	0.10 max	0.04 max	0.012 max	0.65–0.85		0.006–0.016	97.98
Zn–Cu–Ti	0.003–0.30	0.007–0.02 max	0.002–0.012 max	0.50–0.90	0.08–0.16		98.61
Zn–Al–Mg	0.002–0.003 max	0.002–0.003 max	0.002–0.003 max	0.002 max		0.03–0.07	99.81
Zn–HiAl, superplastic	0.003 max	0.003 max	0.003 max	0–0.6		0–0.03	75.36
						20–24	

capacity of a few tons. The more highly alloyed compositions are more effectively melted and mixed in low frequency induction furnaces. The furnace must be refractory-lined to eliminate iron pickup by the molten metal. The metal temperature is maintained $<500^{\circ}\text{C}$ to minimize loss by oxidation. A ladle is used to transfer the metal for casting into molds; the pouring temperature is usually $\sim 440^{\circ}\text{C}$. Zinc scrap is not generally suitable for remelting because it may contain undesirable impurities.

Although more and more zinc sheet and strip are produced in continuous mills, some is still produced by rolling slabs cast in open or closed book-type molds made of cast iron (124,125). The casting temperatures are between 440 and 510°C , mold temperatures between 80 and 120°C . The contact surfaces of the mold must be smooth and clean to allow unrestricted shrinkage of the cast slab. Mold lubricant is not necessary, but if used should be held to a minimum. Slabs cast in open molds must be skimmed immediately to remove surface oxide. Rolling slabs are cast $1.87\text{--}10$ cm thick.

Zinc rolling slabs have been cast successfully by semicontinuous direct-chill casting methods. This is the preferred method for superplastic zinc alloys which, because of their large freezing range, display unacceptable surface shrinkage when cast in open molds.

The open-mold cast slabs are preheated to $150\text{--}260^{\circ}\text{C}$ for initial rolling in rough or breakdown mill. Composition of slab influences the temperature employed. Special high grade or high grade is used to avoid the harmful effect of impurities. Tin should be absent altogether, because its presence at concentrations of 0.004% can cause the zinc to crumble at hot working temperatures. Slabs for strip are reduced by longitudinal rolling to a thickness convenient for coiling, generally < 2.5 mm. For sheet, slabs are rolled laterally until the desired width is obtained. Then the sheets are turned 90° and rolled to a thickness two to four times the final gauge. By cross-rolling, the slab is worked in two directions, reducing to some degree the effects of anisotropy.

Strip is produced as wide as 2 m and in thicknesses as low as 0.1 mm in regular mills. Foil in thicknesses of 0.025 mm or less is produced in special mills. To obtain strip with a bright surface, high ductility, and low hardness, finish rolling is performed hot at $120\text{--}150^{\circ}\text{C}$.

Zinc sheet is produced by the pack-rolling process, in which $2\text{--}40$ rough-rolled sheets are stacked together in packs and rolled simultaneously. Packs must be split frequently, interchanging inner and outer sheets to equalize temperatures and reductions. With care, good quality sheets can be produced by this technique, but considerable variations in properties can occur. If a bright ductile product is desired, rolls are held at $120\text{--}150^{\circ}\text{C}$; the reduction on the last pass is $20\text{--}40\%$.

Lubrication of sheet and strip is necessary for all operations. Although for special operations vegetable and mineral oils may be employed, a mixture of paraffin and tallow oil is normally preferred in rough rolling. Requirements for finish-roll lubricant are more strict because of staining caused by breakdown of the oil or reaction with the zinc. Strip zinc is usually finish-rolled with cotton seed or mineral oil.

In recent years, much attention has been given by the zinc industry to the development of methods for casting and rolling the metal continuously

(126–128). The Hazelett casting machine employed consists essentially of two continuous steel belts, supported and driven through a system of pulleys (129). These form the walls of the mold, which is closed at the sides by sets of small steel blocks linked together by cables forming two endless chains sandwiched between the belts. Molten metal is fed from a tundish or funnel into the cavity between the belts, which are cooled by water sprays. The belts are rotated at a controlled speed and, as the metal solidifies, the slab is drawn downward, thus producing a continuous cast ingot; its thickness can be varied from 10 to 75 mm by adjusting the belt separation. Owing to the continuous nature of the casting operation, the grain size of the solid slab is much finer than when static molds are used, and subsequent reduction in the rolling mill is therefore easier, giving a more uniform product.

After leaving the casting machine, the slab is cooled by water sprays to 180–240°C and fed into the mill, which is generally of the four-high roll type, where a 60% reduction is taken in one pass. The strip is then coiled and, when the casting run has been completed, is fed back through the mill and rolled at a temperature of 80–90°C, with a reduction up to 50%, to give the required final thickness, finish, and properties.

Zinc sheet and strip can be easily fabricated by drawing, spinning, bending, stamping, coining, embossing, blanking, and impact extrusion. Rolled-zinc products in the form of strip, sheet, wire, and rod have many and varied commercial applications. Strip is formed into dry-cell battery cans, mason jar covers, organ pipes, grommets, eyelets, and many other objects, some of which are subsequently brass or chromium plated (jewelry, medallions, bathroom accessories, etc) (130). The zinc–carbon dry-cell application accounts for about one-half of the rolled-zinc consumption in the United States (see BATTERIES). Sheet zinc is used in photoengraving and also in the construction of roofing and other architectural uses. Special high grade zinc with a maximum iron content of 0.0014% in the form of plate and rods gives cathodic protection to steel in marine and pipeline applications.

The low creep resistance of unalloyed zinc sheet and strip is one of its most serious defects and restricts its application. Strip made with Zn-0.6 Cu-0.10 Ti composition has superior creep resistance and is used in structural applications where high, continuously applied stresses are encountered in service.

A new large tonnage application for strip zinc has developed from the decision in 1982 of the U.S. Mint to replace the solid copper (95% Cu-5% Zn) penny with a less expensive copper-plated penny made from zinc strip (Zn-0.8% Cu alloy) (131,132). Zinc blanks stamped from the Hazelett-cast rolled zinc are barrel-plated with copper prior to coining to produce the finished penny. In 2003, ~22,000 Mt of special high grade zinc were used to make 9.1 billion pennies.

Another commercial development of the 1970s is the application of superplasticity that is exhibited by a number of zinc alloys (133–136). Under the right conditions, the material becomes exceptionally soft and ductile and, under low stresses, extensions exceeding 1000% can be obtained without fracture. The grain size must be extremely small (~1 μm) and stable. This grain size is less than one-tenth that of common metals in the wrought condition.

Extremely fine-grained two-phase structures can be developed in zinc–aluminum eutectoid alloys (~22% aluminum with and without minor alloying

additions) by rapid quenching from above the eutectoid temperature of 275°C or by rolling to appreciable degrees of deformation at somewhat lower temperatures, or both. If sheet with this fine-grained structure is heated to just below the transformation temperature of 245–270°C, optimum superplastic behavior is obtained. Because of the ductility and low strength in this condition, the material is similar to thermoplastic polymers and, similarly, can be molded into complex shapes by various processes. When cooled to room temperature, its strength and hardness are many times greater than those of any thermoplastic. Tensile strengths of the superplastic zinc alloys at room temperature range from 190 (28,000) for the binary alloy to 380 MPa (55,000 psi) with the higher alloy compositions. A simple postforming heat treatment can increase strength to 350–440 MPa (51,000–64,000 psi). These alloys can be molded easily like thermoplastics at moderately elevated temperatures, but at room temperature have normal metallic properties, including strength, stiffness, conductivity, and stability, which no plastic can equal. The tooling cost is generally considerably lower than for conventional pressing, which is particularly beneficial for limited production runs (10,000 parts or less).

Parts made from these materials are formed from sheet metal, or solid, three-dimensional metal preforms (137). Complex housings, bezels, and equipment covers are typical of the former. Applications involving solid shapes include gears, pulleys, flywheels, and similar parts.

10.5. Zinc Dust and Powder. Zinc dust and powder are particulate forms of zinc that have many interesting and useful applications (2). The terms dust and powder have been used more or less indiscriminately to designate particulate zinc materials. Here, the term zinc dust designates material produced by condensation of zinc vapor, whereas zinc powder indicates the product obtained by atomizing molten zinc. Zinc dust is manufactured by vaporizing zinc from a suitable source material. The vapor is condensed under conditions which permit control over purity and fineness (138–140). The zinc vapor emanating from a boiler is led into a condensing chamber where it is diluted with inert gases and quickly chilled. The frozen droplets or dust are collected at the bottom of the condenser, screened, and packaged. The purity of the zinc dust depends on the source material or charge to the zinc boiler.

In the atomizing process, a stream of molten zinc is broken into tiny droplets by the force of a pressurized fluid impinging on the stream. The fluid can be any convenient material, although air is normally used. The atomized drops cool and solidify rapidly in a collection chamber. The powder is screened to specified sizes. Particulate zinc is also produced by other methods, eg, electrolytic deposition and spinning-cup techniques, but these are not of commercial importance.

Zinc dust is smaller in particle size and spherical in shape, whereas zinc powder is coarser in size and irregular in shape. The particle size of zinc dust, important in some applications, is controlled by adjusting the rate of condensation. Rapid cooling produces fine dust, slower condensation coarse dust. In the case of zinc powder, changes in the atomization parameters can be employed to change particle size to some degree. The particle size distributions for commercial zinc powders range from 44 to 841 μm (325–20 mesh). The purity of zinc powders is 98–99.6%.

ASTM recognizes two types of zinc dust in specification ASTM D 520-51 (reapproved 2000) (141), which includes permissible impurity concentrations. The metallic content of most commercial grades is 95–97%. The zinc oxide content is between 3 and 5%; finer dusts contain higher concentrations because of high surface areas. Zinc dusts are manufactured in various size ranges, and a typical commercial dust has an average particle diameter between 4 and 8 μm . Usually, dusts are screened to be essentially free of particles coarser than 75 μm (200 mesh).

A major use of zinc dust is in paint coatings (see Table 18). Zinc-dust paints can be classified into those containing zinc oxide as a substantial portion of the pigmentation and those in which zinc dust represents most of the pigment. In the latter, the zinc-dust concentration in the dry paint film is high enough to provide galvanic protection to an iron or steel substrate similar to a galvanized coating (142,143). These paints are classified as zinc-rich paints, and represent one of the fastest growing new markets for zinc in recent years. Such paints are used to supplement galvanized steel for automotive underbody protection against corrosion (144), bridges and other structures, ship hulls, and buildings (2,145,146). Zinc-rich paint is recommended whenever conventional galvanizing is not suitable.

Zinc dust is used in the sherardizing process where work pieces are tumbled with zinc dust in rotating steel drums that are heated electrically or by gas to 370–420°C (147). The steel parts are uniformly coated with zinc. In the chemical and metallurgical industries, zinc dust is used as a reducing agent, in the manufacture of hydrosulfite compounds for the textile and paper industries, and to enhance the physical properties of plastics and lubricants (2).

By far, the largest application of zinc powder is for solution purification in electrolytic zinc plants. This application consumed an estimated 17,700 t of

Table 24. Other Metals in North American Zinc Concentrates

Metal	Percent ^a	Process step	
		Electrolytic	Pyrometallurgical
lead	0.2–6.0	leach residue	sinter fume, refining column, ISF lead bullion and copper dross
copper	0.1–2.8	leach residue, purification residue	retort residue, ISF lead bullion and copper dross
cadmium	0.1–0.8	purification residue	sinter fume, refining column
silver	27–1900 ^b	leach residue	retort residue, ISF lead bullion and copper dross
gold	0.3–12 ^b	leach residue	retort residue, ISF lead bullion and copper dross
mercury	0.001–0.03	roaster off-gas	roaster off-gas
germanium	0.004–0.04	leach residue	sinter fume
gallium	0.005–0.02	leach residue	retort residue
indium	0.01–0.03	leach residue	sinter fume, refining column
thallium	trace	leach residue	sinter fume

^aUnless otherwise indicated.

^bg/t.

powder in 1980. Zinc powder is also used in primary batteries, frictional materials, spray metallizing, mechanical plating, and chemical formulations.

11. By-Product Metals

Ores that are exploited primarily for zinc invariably contain one or more other valuable metals. Various ores contain different combinations of such other metals (see Table 24). For examples, eastern ores commonly contain only cadmium as a significant recoverable value.

Cadmium and mercury are usually recovered in separate processes at the zinc plant. The others are shipped as enriched residues to plants that specialize in their recovery.

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