LEAD AND LEAD ALLOYS

1. Introduction

Lead [7439-92-1], Pb, is an essential commodity in the modern industrial world, ranking fifth in tonnage consumed after iron (qv), copper (qv), aluminum (see ALUMINUM AND ALUMINUM ALLOYS), and zinc (see ZINC AND ZINC ALLOYS). More those half of the lead produced in the world now comes from recycled sources (see RECYCLING, NONFERROUS METALS).

Lead has outstanding properties: low melting point, ease of casting, high density, softness, malleability, low strength, ease of fabrication, acid resistance, electrochemical reaction with sulfuric acid, and chemical stability in air, water, and earth. The principal uses of lead and its compounds lead-acid batteries. For most applications, lead is not used in its pure state, but rather as an alloy (see LEAD ALLOYS).

Lead, copper, silver, and gold were the metals first used by ancient humans. The Egyptians probably used lead as early as 5000 BC. Simplicity of reduction from ores, low melting point, and ease of fabrication presumably led to its use. Lead was also widely used by the Greeks and Romans. Segments of the fluted columns common to Greek architecture are pinned together by iron rods fitted into sockets which were filled with molten lead. Lead water pipes have been found in the ruins of Rome and Pompeii, confirming the use of lead in antiquity. Some pipes of this period still function in Britain.

Use of lead in modern industrial society results from its unique physical and chemical properties. By the middle of the nineteenth century, world production of lead had risen to 1×10^5 metric tons per year, passed 1×10^6 t/yr early in the twentieth century, and reached 1.5×10^6 t/yr by midcentury. Lead mine production reached 3.2×10^6 t in 2004.

Lead and its compounds are cumulative poisons and should be handled with recommended precautions. These materials should not be used in contact with food and other substances that may be ingested (see also LEAD COMPOUNDS, INDUSTRIAL TOXICOLOGY).

2. Occurrence and Ores

In comparison to aluminum and iron, the most abundant metals in the earth's crust, lead is a rare metal. Even copper and zinc are more abundant by factors of five and eight, respectively. However, the occurrence of concentrated and easily accessible lead ore deposits is unexpectedly high, and these are widely distributed through the world. The most important ore mineral is galena [12179-39-4], PbS (87% Pb), followed by anglesite [7446-14-2], $PbSO_4$ (68% Pb), and cerussite [14476-15-4], $PbCO_3$ (77.5% Pb). The latter two minerals result from the natural weathering of galena.

Galena is found in fissure veins and replacement bodies, and may be associated with sphalerite (zinc sulfide), pyrite (iron sulfide), marcasite, chalcopyrite, tetrahedrite, cerussite, anglesite, dolomite, calcite, quartz, and barite, as well as the valuable metals gold, silver, bismuth, and antimony. The formation of lead ore deposits is thought to have occurred during the emplacement of igneous

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rock masses with the solidification of silicates from molten magma. Components of the molten magma, such as metal sulfides, were concentrated in the liquid remaining from the crystallization and forced by the pressure from the growing silicate rocks into available channels such as fault fissures.

Most (97%) lead mined in the United States comes from mines in Missouri and Alaska. The rest comes from mines in Colorado, Idaho, Montana, Washington, and Nevada. Ores of the Southeast Missouri lead belt and extensive deposits such as in Silesia and Morocco are of the replacement type. These deposits formed when an aqueous solution of the minerals, under the influence of changing temperature and pressure, deposited the sulfides in susceptible sedimentary rock, usually limestone and dolomites. These ore bodies usually contain galena, sphalerite, and pyrite minerals, but seldom contain gold, silver, copper, antimony, or bismuth.

Lead and zinc minerals are so intimately mixed in many deposits that they are mined together and then separated. Silver minerals are frequently found in association with galena.

The concentration of lead in ore bodies of commercial interest generally ranges from 2 to 6%; the average is 2.5%. Improvements in ore-dressing techniques have made possible the exploitation of deposits having lead contents even less than 2%.

The world reserves of lead are estimated at 67×10^6 t and scattered around the world (1). The recovery of lead from scrap is of prime importance in supplying U.S. demands so that the entire reserve base is estimated at 120×10^6 t. Total world resources are estimated at 1.4×10^9 t. See Table 1 for world mine production, reserves, and reserve base (1).

3. Physical Properties

Lead, atomic number 82, is a member of Group 14 (IVA) of the Periodic Table. Ordinary lead is bluish grey and is a mixture of isotopes of mass number 204 (15%), 206 (23.6%), 207 (22.6%), and 208 (52.3%). The average atomic weight of lead from different origins may vary as much as 0.04 units. The stable isotopes are products of decay of three naturally radioactive elements: ^{206}Pb comes from the uranium series (see URANIUM AND URANIUM COMPOUNDS), ^{208}Pb from the thorium series, and ^{207}Pb from the actinium series (see ACTINIDES AND TRANSACTINIDES). The crystal structure of lead is face-centered cubic; the length of the edge of the cell is 0.49389 nm; the number of atoms per unit cell is four. Other properties are listed in Table 2.

4. Chemical Properties

Lead forms two series of compounds corresponding to the oxidation states of +2 and +4. The +2 state is the more common. Compounds of lead(IV) are regarded as covalent, those of lead(II) as primarily ionic. Lead is amphoteric, forming plumbous (Pb(II)) and plumbic (Pb(IV)) salts as well as plumbites and plumbates, respectively.

Lead is one of the most stable of fabricated materials because of excellent corrosion resistance to air, water, and soil. An initial reaction with these elements results in the formation of protective coatings of insoluble lead compounds. For example, in the presence of oxygen, water attacks lead, but if the water contains carbonates and silicates, protective films or tarnishes form and the corrosion becomes exceedingly slow.

Because of its position relative to hydrogen in the electromotive series, theoretically lead should replace hydrogen in acids. However, the potential difference is small and the high hydrogen overvoltage prevents replacement. Reaction with oxidizing acids releases oxidants which combine with hydrogen to depress the overvoltage, resulting in replacement.

4.1. Acid Oxidation.   Reactions of lead with acid and alkalies are varied. Nitric acid, the best solvent for lead, forms lead nitrate; acetic acid forms soluble lead acetate in the presence of oxygen; sulfuric acid forms insoluble lead sulfate. Sulfuric acid is stored in containers with chemical or acid-grade lead. Lead dissolves slowly in HCl, but in the presence of aqueous alkalies forms soluble plumbites and plumbates.

There are three common oxides of lead. Lead oxide [1317-36-8], PbO, also known as litharge, is formed by heating lead in air or blowing air into molten lead. It is used in batteries (qv), glass (qv), and ceramics (qv). Lead tetroxide [1314-41-6], Pb_3O_4, is formed by controlled oxidation of litharge at about $450°C$, and lead dioxide [1309-60-0], PbO_2, is formed by electrolytic oxidation of lead salts or by strong oxidizing agents. Lead dioxide is used in the manufacture of dyes (see DYES AND DYE INTERMEDIATES), rubber substitutes, and pyrotechnics.

5. Processing

Lead is usually processed from ore to refined metal in four stages. These are ore dressing, smelting, drossing, and refining (see MINERALS RECOVERY AND PROCESSING).

5.1. Ore Dressing.   The principal lead mineral, galena, in most crude ores, is separated from the valueless components, or gangue. Other valuable minerals that are present in the ore may be recovered either together with the lead, or in a separate step (2,3). Occasionally, the ores are sufficiently rich in lead and low in impurities to be smelted directly.

The principal steps in ore dressing are crushing, grinding, and concentration (beneficiation) (Fig. 1). Crushing and grinding, collectively called size reduction (qv) or comminution, of the mined ore are necessary to liberate the galena and other desired minerals from interlocking gangue, and also to bring the ore to the size appropriate for the concentration step. Size reduction is carried out in stages. Primary (gyratory or jaw) crushers receive the mined ore, and the product is fed to the secondary (cone or roll) crushers. Sometimes tertiary crushers are used. Vibratory screens separate the finer material in the crusher products and allow return of the oversized pieces for further crushing. Finer size reduction is accomplished by wet grinding in horizontal tumbling mills containing steel grinding media: rods for the first stage grind, and balls for the second. Autogenous grinding, wherein the large lumps of the ore itself are used as the grinding

media, is employed occasionally. The finer (≤ 0.2 mm) fraction of the grinding mill discharge is separated using either mechanical (rake or spiral) classifiers or the more widely used hydrocyclone. The coarser fraction is fed back for further grinding.

Gravity concentration, ie, the separation of ore from gangue based on the differences in specific gravities, using jigs, heavy–medium separators, or spiral concentrators for example, is applicable for lead ores. However, the predominant beneficiation technique used in modern plants is the bubble or froth flotation (qv) process (4,5).

In froth flotation, the fine ore slurry is discharged to a conditioning tank in which it is mixed with frothers. It is then passed to the flotation cells where air is pumped up through the slurry, forming bubbles to which the selected mineral, eg, galena, adheres. The mineralized bubbles rise and accumulate as an ore-laden froth bed. A concentrate is obtained by skimming the froth from the cell. The adherence to the air bubbles, and therefore the recovery of selected minerals, depends on the action of the following types of reagents.

Collectors are the most important class of reagents in froth flotation. These selectively bind to the surface of a selected ore mineral particles to render the particles hydrophobic (water repellant). Collectors are heteropolar organic molecules having a reactive polar group and a nonpolar, hydrophobic hydrocarbon tail. The polar group reacts and adsorbs on the surface of the target mineral, forming a one molecule thick, water repellant film. The water repellency is conferred by the tail of the collector, and causes the ore particles to preferentially adhere to air bubbles. Xanthates are the most common collector used in galena flotation.

Depressants are reagents that selectively prevent the reaction between a collector and a mineral, thus preventing its flotation. For example, sodium cyanide [143-33-9] depresses sphalerite [12169-28-7] (zinc sulfide) and pyrite [1309-36-0] (iron sulfide) but not galena. It thus enhances selective flotation of the galena.

Activators promote the reaction of the collector with some minerals. For example, ordinarily xanthates do not bind to sphalerite, but pretreatment of the sphalerite using copper sulfate enables it to adsorb the xanthate. Thus it is possible to float the sphalerite from lead–zinc ores after the galena has been recovered.

Frothers such as pine oil [8006-88-0], cresylic acid [1319-77-3], polyglycols, and long-chain alcohols stabilize the mineralized froth bed long enough for it to be gathered. Conditioners are used for pH control which is important in flotation. If the pH of the slurry is too high, the hydroxyl ion competes with the xanthate. If the pH is too low, xanthates become insoluble. A lead flotation slurry should be slightly alkaline. The pH is adjusted, when necessary, using sodium carbonate or calcium oxide.

The lead concentrate from rougher flotation cells is upgraded by additional flotation steps. The final concentrate is dewatered by settling in thickeners to a moisture content of 50%. Vacuum filtering further decreases the moisture level to 15%.

If sphalerite is present in the ore the tailings from the lead flotation cells are discharged to another conditioner where copper sulfate is added and then fed to the zinc flotation cells. The final tailings are discarded as waste.

The analysis of partially dried lead concentrate, ready to be treated in a series of processes to produce a commercial grade of lead, is presented in Table 3.
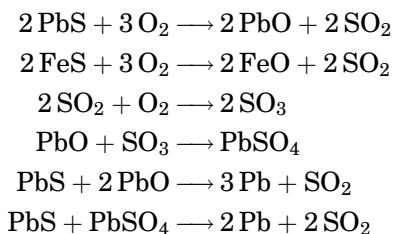
5.2. Smelting. Since the late 1800s the smelting of lead has been dominated by sinter-blast furnace technology adopted from the iron and steel (qv) industries, and in the early 1960s the Imperial smelting furnace (ISF) was developed to handle mixed lead–zinc concentrates. Several newer technologies, from work in the 1970s, 1980s, and 1990s, have been developed to directly smelt lead ores and bypass the sintering process. Some of these technologies, ie, the Kivcet, Isasmelt, and Queneau, Schumann, Lurgi (QSL), came into commercial operation in the 1980s, but sinter-blast furnace and ISF processes are still dominant worldwide.

Blast-Furnace Smelting. Sintering. The charge for sintering is prepared by blending selected concentrates, smelter by-products, returned sinter, flue dust, and when required, additional fuel such as coke breeze. The blend is then pelletized in preparation for sintering.

The blended charge is conditioned in a rotating pug mill where water is added to bring the moisture content between 6 and 8%. The feed is then pelletized (0.5 cm in size) in a disk or drum pelletizer.

A typical up-draft sinter machine (Fig. 2) has an endless belt of malleable iron pallets with grate bottoms upon which the charge is evenly spread. Beneath the pallets, wind boxes produce an up-draft of air through the charge. At the feed end, an ignition box starts the roasting. The combustion products, mostly SO_2 and SO_3, are collected, usually for sulfuric acid production.

The sintering operation takes place at approximately 600°C and involves the following reactions:

$$2\,PbS + 3\,O_2 \longrightarrow 2\,PbO + 2\,SO_2$$
$$2\,FeS + 3\,O_2 \longrightarrow 2\,FeO + 2\,SO_2$$
$$2\,SO_2 + O_2 \longrightarrow 2\,SO_3$$
$$PbO + SO_3 \longrightarrow PbSO_4$$
$$PbS + 2\,PbO \longrightarrow 3\,Pb + SO_2$$
$$PbS + PbSO_4 \longrightarrow 2\,Pb + 2\,SO_2$$

The oxides combine with silica [7631-86-9] and form low melting complex silicates that tend to bind the concentrate particles together; for example

$$PbO + SiO_2 \longrightarrow PbO \cdot SiO_2$$
$$FeO + SiO_2 \longrightarrow FeO \cdot SiO_2$$
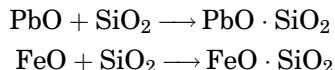
Some lead oxide is reduced by carbon or carbon monoxide, as shown.

$$2\,PbO + C \longrightarrow 2\,Pb + CO_2$$
$$PbO + CO \longrightarrow Pb + CO_2$$
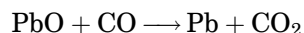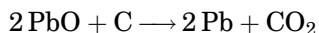
The details of specific plant operations have been well documented (6).

Smelting. In the blast furnace (7), lead and other metal oxides, not reduced during sintering, are reduced to metals; the molten lead is coalesced in the hearth; and the gangue material is separated into a molten slag. The molten lead serves as a solvent for the valuable metallic impurities that are recovered during the refining process, separated, and ultimately purified for marketing. The contaminating oxides, silicates, and sulfides are removed by reagents that induce formation of stratified liquid phases, ie, slag, matte, and speiss in the crucible.

A typical slag (specific gravity 3.6) contains complex silicates of iron, calcium, zinc, magnesium, and aluminum oxides. The quantity of fluxes (compounds added to lower the melting point) added depends on the feed composition, and is calculated to ensure a fluid slag at the operating temperature.

Lead smelters often treat both ores and zinc-plant residues high in zinc oxide content. The zinc oxide is collected in the blast-furnace slag, and can be subsequently recovered in a slag-fuming furnace. Lead is unavoidably entrapped in the slag, therefore its volume should be kept to a minimum. Slags are classified according to the ratio of calcium oxide to iron oxide, and are identified as quarter, half, or one to one.

Copper is frequently a main impurity in blast-furnace charges, and its limited solubility in molten lead as copper sulfide requires that the excess be removed by chemical reaction with components of the charge. For this reason enough sulfur is left in the sinter to form a copper sulfide matte layer having a specific gravity of 5.2.
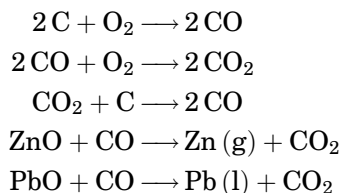
If antimony and arsenic are present in the feed, copper and iron react to form the respective antimonides and arsenides known as speiss (specific gravity 6.0). If it is preferred to remove copper in a speiss layer, the sulfur in the sinter must be reduced and the addition of scrap iron may be necessary to encourage speiss formation. Matte and speiss are usually sent to a copper smelter for recovery of the metals.

The contents of the crucible are tapped through a Roy tapper (8, 9) into external settlers for layer separation. The tapper removes blast furnace products as they are made, giving a more uniform blast-furnace performance. A typical bullion analyzes in wt%, 1.0–2.5 Cu, 0.6–0.8 Fe, 0.7–1.1 As, 1.0–3.0 Sb, 0.01–0.03 Bi, 0.2 Ag, and 0.0003 Au. A typical blast furnace slag contains 25–33 wt% FeO, 10–17 wt% CaO, 20–22 wt% SiO_2, 1–2 wt% Pb, and 13–17 wt% Zn. A section across the width of the blast furnace is shown in Figure 3.

Imperial Smelting Process. The Imperial smelting process has been well documented (10,11). This smelting process is used particularly for mixed zinc–lead ores, when the mineralization is such that separation of the lead and zinc portions is difficult. High grade galena concentrates and oxidized lead ores also can be added to the charge. Feed material is often a sinter of mixed zinc–lead concentrates, zinc blende [12169-28-7], and galena concentrates. Recoveries

from concentrate to slab zinc and salable lead are 90–93% and 92–94%, respectively. (see. Fig. 4).

The essential reactions taking place for smelting are

$$2\,C + O_2 \longrightarrow 2\,CO$$
$$2\,CO + O_2 \longrightarrow 2\,CO_2$$
$$CO_2 + C \longrightarrow 2\,CO$$
$$ZnO + CO \longrightarrow Zn\,(g) + CO_2$$
$$PbO + CO \longrightarrow Pb\,(l) + CO_2$$

The furnace charge consists of zinc–lead sinter, metallurgical coke, and recirculating metallic drosses and flux. The charge cycle is fully automatic.

Blast air, preheated to 650°C, is delivered by centrifugal blowers through a refractory-lined bustle main to the furnace. Zinc vapor from the reduced sinter is carried out with the furnace gases to a condenser fitted with mechanical rotors that are partly immersed in a shallow pool of molten lead. The lead flows countercurrently to the gas and is vigorously agitated by the rotors to create an intense shower of lead droplets throughout the condenser.

The furnace gases are shock-cooled by the lead spray. The zinc is cooled rapidly through the critical temperature range in which zinc vapor reverts to zinc oxide. The liquid zinc is taken up by the lead. The remaining gases pass to a wet scrubber system for the removal of suspended oxides of lead and zinc called blue powder. The lead-containing zinc flows to an external separation system. The slag and molten lead are tapped intermittently into a forehearth where the lead bullion is separated from the slag by a syphon. The slag flows to a cast-iron launder and is granulated.

The lead and zinc are separated into two molten phases by progressive cooling. Following ammonium chloride treatment to remove dross, the lead is returned to the condenser. Zinc is cast into ingots after dissolved lead is removed by cooling.

Other Lead Smelting Processes.   Stricter regulations concerning lead emissions and ambient lead in air levels (see AIR POLLUTION), and the necessity to reduce capital and operating costs have encouraged the development of alternative lead smelting processes to replace the sinter plant–blast furnace combination.

Four lead smelting processes have reached the stage of being promoted as commercially viable for lead concentrates (Table 4). In general these processes offer the following potential advantages: ability to meet proposed future in-plant hygiene requirements; reduction in energy costs through the utilization of the heat of combustion of the concentrates; reduction in capital and operating costs through the use of compact, high intensity vessels; and the production of low volumes of process gas of high SO_2 content through the use of large amounts of (tonnage) oxygen.

Kivcet Process.   The Kivcet process (12) is based on the roasting–smelting of the lead-bearing charge in an oxygen atmosphere, and in the formation of sulfur dioxide gas and an oxide smelt. The oxide smelt is reduced by means of

an agent such as coal (qv) or coke, to produce lead. Zinc can also be recovered as zinc oxide by fuming the slag.

These operations are all conducted in the single unit of the Kivcet furnace, which consists of a smelting shaft, gas removal shaft, and electrothermic part. A schematic of the Kivcet process is shown in Figure 5 (13). The electrothermal part is separated from the smelt shaft in the gas space by a partition wall which is partially immersed into the smelt. Raw materials are received from the stockpile, proportioned, mixed, and dried in the rotary drier before being fed into the furnace. The furnace charge is dispersed by oxygen.

Ignition of the charge takes place in this oxygen atmosphere. Melt material is reduced during its passage through the layer of reducing agent floating on the metal bath. The reducing agent is fed into the furnace with the lead-bearing charge. Metallic lead resulting from reduction settles at the bottom of the furnace.

Gases generated in the charge roasting are rich in sulfur dioxide, and contain metal oxide vapors and high metal dust concentrations. The gases are cooled in a waste heat boiler installed above the gas removal shaft. During the cooling, the sulfur dioxide reacts with the metal oxides to form the corresponding metal sulfates.

Cooled dust-laden gas is dedusted in an electrostatic precipitator and sent to the cleaning unit to remove impurities such as arsenic, fluorine, and chlorine before being sent on to the sulfuric acid production plant.

In the electrothermic part of the furnace, electrical energy introduced via three carbon electrodes, keeps the bath molten and completes the lead oxide reduction. Fumes generated in the electrothermic section are oxidized in a post-combustion chamber by adding ambient air, before the vapor is cooled, dedusted, and released to the atmosphere.

The cooling of gases is performed in a vertical tube-type exchanger, and the hot air produced is used as a heating medium in the charge drying unit. Fumes having lead and zinc oxides are trapped in the heat exchanger and dedusting equipment. These dusts are normally treated in an electrolytic zinc plant.

Crude lead flows continuously from the Kivcet furnace through a syphon and is sent to two kettles where some copper, in dross form, is separated and subsequently processed; the lead bullion is cast into one ton ingots. Slag is tapped intermittently from the furnace through a sidewall tapping hole and sent to a slag granulation unit before being discharged for disposal.

For environmental reasons, the entire process is handled by enclosed equipment. Lead recoveries of 96% can be obtained from the raw materials, and sulfur dioxide gas released in the process is used to produce sulfuric acid.

QSL Process.   The QSL process (14) is a continuous single-step process having great flexibility in regard to the composition of the raw materials. In this process the highly exothermic complete oxidation, ie, the roasting reaction, can be avoided to some extent in favor of a weakly exothermic partial oxidation directly producing metallic lead. However, the yield of lead as metal is incomplete due to partial oxidation of lead to lead oxide.

The remaining lead must be oxidized and later can be reduced from the slag using carbon. The ratio of metallic lead to lead oxide which depends in part on the type of raw materials to be processed, can be adjusted within certain limits by

varying the degree of oxidation. In treating lead-rich concentrates having a lead content of approximately 70%, more than 75% of the lead can be obtained directly as metallic lead.

The entire QSL process takes place in a single reactor as shown in (15). The reactor consists of an almost horizontal, refractory-lined cylinder, which can be tilted by 90° when operation is interrupted. Concentrates, fluxes, recirculated flue dust, and normally a small amount of coal, depending on the type of concentrate, are pelletized. The pelletizer ensures that the raw materials are mixed to the required degree of uniformity.

The moist green pellets, easier to handle than the nonagglomerated dusty material, are charged at the reactor top into the oxidation zone without further treatment. The pellets fall into a melt mainly consisting of primary slag. Tonnage oxygen is blown into the melt through submerged gas-cooled bottom nozzles called Savard-Lee injectors. The roasting reactions take place at 1000–1100°C, producing metallic lead, primary slag with a high (30%) content of lead oxide, and an off-gas rich in sulfur dioxide.

The lead bullion, ie, crude metallic lead, is discharged via a syphon, a gastight seal, whereas the primary slag passes into the reduction zone separated from the oxidation zone by a weir. Pulverized coal (qv) is injected into the reduction zone from the bottom by carrier air, and some is burnt by oxygen using the same injectors. The lead contained in the primary slag is gradually recovered by reduction. The low lead final slag is tapped and discarded or further processed to recover zinc. The lead settles to the bottom of the reduction zone and flows back into the oxidation zone to recombine with the primary lead bullion.

The QSL process yields only a small off-gas volume having a high concentration of sulfur dioxide owing to the use of tonnage oxygen. The combined off-gas from reduction and oxidation leaves the reactor through a vertical uptake at 1100–1150°C. The uptake, part of the waste heat recovery system, cools the off-gas to approximately 750–800°C. The process gas passes through a waste heat boiler for further cooling and a hot gas electrostatic precipitator for dedusting before being transferred to the sulfuric acid plant.

The combined flue dust from waste heat boiler and electrostatic precipitator, including dust from the ventilation system, is collected in a bin and recirculated to the mixing and pelletizing step, where it is used as a binding reagent.

Boliden's Kaldo Process. The top blown rotary converter (TBRC) (16) is a highly flexible metallurgical unit which has been incorporated into processes producing steel, copper, and nickel. In the early 1970s Boliden Metall AB began work to adapt Kaldo technology to the treatment of lead-bearing dusts and later the smelting of lead concentrates (Fig. 7).

Dried lead concentrate, flux, and return dust are added to the converter through a lance during the smelting cycle. Oxygen enriched air is injected at the same time to carry out the smelting reactions and maintain the temperature. Once smelting is completed, the air is shut off and the reduction carried out using an oxygen–fuel mixture fed through the lance system. This is a batch process where both smelting and reduction are carried out in the same vessel. After reduction, slag having less than 3% Pb is skimmed for disposal. The slag contains most of the zinc in the charge and could be transferred to a slag fuming plant for

recovery of zinc and residual lead. Lead bullion is then cast for refining by conventional methods.

Owing to the cyclic nature of the TBRC operation, waste heat recovery from the off-gases is not practical and the SO_2 content of the gas varies with the converter cycle. In order to supply a relatively uniform flow and strength SO_2 gas to a sulfuric acid plant, a system has been installed at Ronnskär whereby the SO_2 from fluctuating smelter gases is partially absorbed in water. During smelter gas interruption, SO_2 is stripped with air and the concentrated gas delivered to the acid plant.

The Kaldo process offers some significant advantages from an emission viewpoint. The reactor can be completely enclosed in a vented enclosure throughout the operating cycle. Operator exposure is then reduced to a minimum because the operation, including charging, slag skimming, and bullion tapping, is controlled from a central control room.

The process is flexible and permits treatment of a wide variety of plant feed materials. Overall lead recovery is in the range of 96–98%. The operation is, however, cyclic which increases the cost of the sulfur fixation plant, and any zinc contained in the concentrate is lost in the slag unless slag fuming is added or already available at the site.

Isasmelt Process.   The Isasmelt process (17) is a two-stage lead smelting process developed jointly by Mount Isa Mines Limited (Mt. Isa) and Commonwealth Scientific & Industrial Research Organization (Australia). In the first stage, lead sulfide concentrates are smelted to form a lead oxide-rich slag, which is then reduced by coal in the second stage to form lead bullion and a discard slag.

The Isasmelt process uses a simple stationary, cylindrical, refractory-lined reaction vessel. The typical blended feedstock to the vessel is of a moist lumpy consistency and this feature greatly simplifies environmental control equipment requirements.

The use of the Sirosmelt lance enables the process to be operated on ambient air or using oxygen enrichment. Coal, coke breeze, and fuel oil have all been demonstrated as viable supplementary sources of energy for smelting or reduction. A schematic diagram of a typical Isasmelt lead smelting process is shown in Figure 8 (18).

Lead concentrate slurry is gravity fed from a stock tank and dewatered on a drum vacuum filter. The resulting filter cake is mixed with silica and limestone fluxes, coke breeze, and recycle fume in a twin-shaft paddle mixer. This agglomerate, containing typically 10% moisture, is fed by conveyor to the smelting furnace where it is dropped directly into the molten slag bath. Coke breeze is used as fuel. Smelting air is injected into the bath through a submerged Sirosmelt lance to fully oxidize the feed and burn the coke. The smelting air is enriched to 30% oxygen or higher to reduce the off-gas volumes so that both furnaces can be operated simultaneously. Smelting temperatures are maintained in the range from 1170 to 1200°C to decrease the heat load on the reduction furnace.

The high lead slag from the smelting furnace is tapped continuously and transferred down a heated launder directly into the reduction furnace through a port in the side of the vessel. Lump coal for reduction is fed continuously to the furnace by conveyor and dropped directly into the bath. Heating for the

endothermic reduction reactions is provided by oil injected down the lance. The combustion air stoichiometry is set at 95% of that required for complete oil combustion. Air is injected into the top of the furnace to afterburn the volatile materials from the coal and provide additional heat to the top of the furnace. Reduction temperatures range from 1170 to 1200°C to maintain slag fluidity.

The crude lead and discard slag from the reduction furnace are tapped continuously through a single taphole into molds. The discard slags have a 1 to 2% lead oxide content and 1 to 2% of lead metal prills (pellets).

The off-gas from each furnace is cooled in an evaporative gas cooler and cleaned in a reverse pulse baghouse before being either vented to atmosphere or used in manufacturing sulfuric acid. The baghouse dust from both the smelting and reduction furnaces is combined and recycled through the smelting furnace.

Outokumpu Lead Smelting Process. The Outokumpu flash smelting process (16), used to treat copper and nickel concentrates, has been adapted to flash smelting of lead concentrates. Extensive pilot-plant testing was carried out in the 1960s and 1970s, but was discontinued primarily because of high fume carryover and associated problems. Tests were run in the mid-1980s after redesign of the uptake. Typical pilot-plant design rate was $3 - 5$ t/h.

The dried charge is pneumatically fed to a burner mounted on the roof of the reaction shaft. Normally oxygen is used to get an autogenous smelt. The off-gases analyze around 70% SO_2 and can be used for the manufacture of sulfuric acid after conventional gas cleaning.

Flash furnace slag containing 20−40% Pb is reduced in an electric furnace using coal injection. Discard slags have 1−3% Pb and $CaO:FeO:SiO_2$ in the ratio of 0.8:1.0:1.0.

5.3. Drossing. The impure lead bullion, produced from any of the smelting processes, is cooled to remove dissolved copper prior to the refining operation. The operation is referred to as copper drossing, and is performed in one or two 250 t cast-iron kettles. The process consists of skimming off the dross, stirring the lead, and reskimming.

The first drossing after the furnace tapping is a rough, high temperature skimming to remove the floating scum on the lead. After this step has removed most of the insoluble dross, the molten lead is transferred to a second kettle in which the temperature is lowered as close to the melting point of lead as practical to further reduce the solubilities of the contaminates, particularly copper. After skimming at this lower temperature, a vortex is created in the lead bath, and sulfur, at a concentration of approximately 10 kg/t lead, is added to the vortex. The sulfur further decreases the solubility of copper. The stirrer is then stopped, and the lead skimmed. The dross should contain from 0.004 to 0.04% copper.

The lead bullion, ready to be shipped to the refinery, contains in solution impurities such as silver, gold, copper, antimony, arsenic, bismuth, nickel, zinc, cadmium, tin, tellurium, and platinum metals. The dross from this operation contains considerable quantities of copper and lead as well as other valuable metals. Separation and recovery is economically imperative. The dross is treated to produce readily separated stratified layers of slag, speiss, matte, and lead. Two processes are primarily used.

Continuous Drossing.   A continuous copper-drossing process was developed and patented by The Broken Hill Associated Smelters Pty. Ltd. (Port Pirie, Australia) (19). A top view of the furnace is shown in Figure 9. The hearth is divided into four compartments by submerged walls of varying heights that do not, however, reach up into the matte layer. These control the movement of bullion and direct it to an external cooling system and discharge pot.

When a ladle of blast-furnace bullion is poured into the furnace, the bullion moves over a submerged wall toward the flue end, and is brought into contact with cooled bullion circulating through the cooling launder; the reduction in temperature leads to copper being rejected as mixed sulfide crystals which float to the top of the bath and are then melted to matte by the burners. As each ladle of blast furnace bullion is charged, an equivalent amount of drossed bullion flows through the discharge channel to the delivery pump pot and is pumped to a 100-t kettle for sulfur drossing.

The success of the process results from the fact that nowhere inside the furnace is heat extracted from the copper-saturated blast furnace bullion through a solid surface. The problem of accretion formation (metal build-up), which has plagued many other attempts to establish a copper drossing operation of this type, does not arise. In the cooling launder, lead-rich matte and slag accumulate on the water-cooled plates, but these are designed so that when they are lifted from the bullion stream, the dross cracks off and is swept into the furnace via the cooled lead pot.

Soda Process.   Use of a soda smelting process for treating copper drosses in the reverberatory furnace increases the copper to lead ratios in the matte and speiss, and allows lower operating temperatures. A flow sheet describing this process is shown in Figure 10.
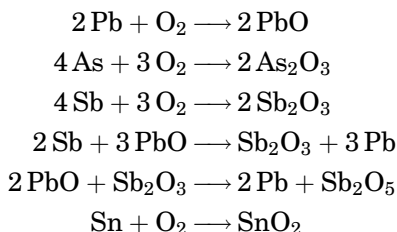
Soda ash, Na_2CO_3; baghouse fume (mostly PbO); coke; and sulfur react to form a low melting matte of sodium sulfide that serves as a collector of iron sulfide. Because no slag formation is required to take care of the iron, the furnace can operate at lower temperatures, just high enough to keep the speiss and matte molten. The reaction of iron and sulfur tends to keep the furnace in good condition and relatively free of magnetite accretions. A comparison of products after drossing using or not using the soda process is shown in Table 5.

5.4. Refining.   *Pyrometallurgical Methods.*   To prepare blast furnace bullion for commercial sale, certain standards must be met either by the purity of the ores and concentrates smelted or by a series of refining procedures (r6–r8,r20,r21). These separated impurities have market value and the refining operations serve not only to purify the lead, but also to recover valuable by-products.

The pyrometallurgical processes, ie, furnace-kettle refining, are based on (*1*) the higher oxidation potentials of the impurities such as antimony, arsenic, and tin, in comparison to that of lead; and (*2*) the formation of insoluble intermetallic compounds by reaction of metallic reagents such as zinc with the impurities, gold, silver and copper, and calcium and magnesium with bismuth (Fig. 11).

Removal by Oxidation.   The oxidizing process used to remove antimony, arsenic, and tin has been termed softening because lowering these impurities results in a readily detectable softening of the lead.

In the furnace/kettle batch process, a charge of drossed blast furnace bullion is treated in a reverberatory furnace or a kettle (see Fig. 12). Oxygen is supplied in the form of compressed air or as lead oxide blown into the bath through submerged pipes. The formation of lead oxide serves by mass action to assure the removal of the impurities to the desired low concentrations. The softening reactions are

$$2\,Pb + O_2 \longrightarrow 2\,PbO$$
$$4\,As + 3\,O_2 \longrightarrow 2\,As_2O_3$$
$$4\,Sb + 3\,O_2 \longrightarrow 2\,Sb_2O_3$$
$$2\,Sb + 3\,PbO \longrightarrow Sb_2O_3 + 3\,Pb$$
$$2\,PbO + Sb_2O_3 \longrightarrow 2\,Pb + Sb_2O_5$$
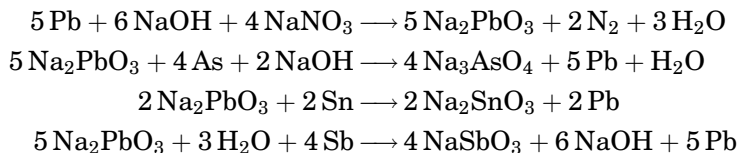$$Sn + O_2 \longrightarrow SnO_2$$

In a typical run on a low hardness charge of 0.3 to 0.5%, after the softening slag from the previous charge has been removed, the bath is agitated by compressed air from pipes extending through the side of the furnace thus softening the bath to 0.03% antimony. This slag has a high oxygen content and is left in the furnace for softening the next batch of lead. The softened lead underneath it is either tapped or pumped to the desilverizing kettle.

The softening of a high hardness charge (3% or greater) follows the same procedure, except that after the first slag is removed, litharge, ie, PbO, is added to hasten the reduction of the hardness to 0.5%. The bath is then blown with air to a concentration of 0.03% antimony.

The continuous softening process used by The Broken Hill Associated Smelters Pty., Ltd. is particularly suitable for lead bullion of fairly uniform impurity content. The copper-drossed blast furnace bullion continuously flows in the feed end of a reverberatory furnace at 420°C, and the softened lead leaves the opposite end at 750°C. Oxidation and agitation is provided by compressed air blown through pipes extending down through the arch of the furnace into the bath.

The continuous removal of the antimony and arsenic into a slag floating on the bath is possible because equilibrium between the lead and the antimony–arsenic-rich slag is rapidly reached at the operating temperature. The rich antimony–arsenic slag overflows through a notch at the flue end of the furnace. A portion of the slag is also discharged at the feed end into an adjacent reverberatory furnace where coke is added to reduce the lead content.

The Harris softening process (21) depends on the interaction of lead, niter [7631-99-4], NaNO$_3$, sodium hydroxide, and the impurities:

$$5\,Pb + 6\,NaOH + 4\,NaNO_3 \longrightarrow 5\,Na_2PbO_3 + 2\,N_2 + 3\,H_2O$$
$$5\,Na_2PbO_3 + 4\,As + 2\,NaOH \longrightarrow 4\,Na_3AsO_4 + 5\,Pb + H_2O$$
$$2\,Na_2PbO_3 + 2\,Sn \longrightarrow 2\,Na_2SnO_3 + 2\,Pb$$
$$5\,Na_2PbO_3 + 3\,H_2O + 4\,Sb \longrightarrow 4\,NaSbO_3 + 6\,NaOH + 5\,Pb$$

The formation of the metallic salts is a pyrometallurgical process, and is commonly referred to as the dry process. The separation of the salts from each other is accomplished by selective dissolution in water, and is named the wet process.

Dry Process.   The softening equipment consists of a 100–225 t kettle in which a reagent cylinder is supported and submerged. The process is carried out in batches. Molten caustic is pumped into the reagent cylinder along with molten lead from the kettle. The latter prevents freezing of the caustic soda. The discharge from the pump is arranged to spray the lead to assure maximum exposure of lead surfaces.

The niter and fresh caustic soda, required to maintain the fluidity of the salt bath in the reactor chamber, are added gradually. When the color of the saturated salts turns from a dark gray to white, the impurity metals are at their highest state of oxidation, and the lead content of the spent salts is very low. In a modification, the arsenic and tin are selectively removed as sodium arsenate and sodium stannate, followed by the removal of antimony as sodium antimonate.

Wet Process.   The sodium arsenate and stannate slag are treated by a leach and precipitation process to produce calcium arsenate, calcium stannate, and a sodium hydroxide solution for recycle. The sodium antimonate filtercake containing selenium, tellurium, and indium is treated in a special metals refinery to recover indium and tellurium.

Removal of Other Impurities.   After softening, the impurities that may still remain in the lead are silver, gold, copper, tellurium, platinum metals, and bismuth. Whereas concentrations may be tolerable for some lead applications, the market values encourage separation and recovery. The Parkes process is used for removing noble metals and any residual copper, and the Kroll-Betterton process for debismuthizing.

In the Parkes process, a quantity (1–2%) of zinc is added to lead which is in excess of the saturation value. This creates insoluble intermetallic compounds consisting of zinc and the noble metals that precipitate from the lead on cooling (22).

This process is a two-step procedure. In the first desilverizing kettle, a high silver–zinc crust is generated by adding to the kettle the low silver crust from the preceding second-kettle desilverizing. This enriching step reduces the amount of zinc per unit of silver to be subsequently recovered, as well as the amount of entrained lead that eventually must be removed in cupelling.

Batch desilverizing is preformed in open steel kettles. The low silver-content crust from the previous charge's second skimming is placed into the first kettles where new, soft lead is pumped. The temperature is raised to approximately 460°C where alloying takes place. A silver-enriched crust forms and rises to the surface. The silver–zinc crust discharged from treating bullion with 0.3% silver content contains about 12% silver. For the second desilverizing step, zinc recovered from the treatment of Parkes crust is added to the melt and stirred in at about 450°C. The quantity of zinc added is calculated to leave less than 3 ppm silver. The kettle is allowed to cool, and the precipitating silver–zinc crystals are skimmed as crust and held for addition to the next charge. The

molten lead, which upon cooling to 320°C is given a final skimming leaving less than 3 ppm silver and copper, is then pumped to the next kettle for dezincing.

The crusts from the Parkes process are then treated to recover the zinc contained in the dross for reuse in desilverizing. This is done by distillation (qv) and more commonly by vacuum technology. The chemistry of this operation is the same as that for batch desilverizing (22,23).

Recovery of Metals from Parkes Crust.   Parkes crust contains significant amounts of zinc and lead which must be recovered in addition to the silver and gold contained in the crust. Until the 1980s this was generally done by first using Faber du Faur-type retorts to distill zinc from the crust, followed by cupellation of the lead–silver metal to produce a litharge slag and doré metal.

In 1986 Britannia Refined Metals (Northfleet, U.K.) introduced technology for the treatment of Parkes crust, a triple alloy of Ag, Zn, Pb, which by 1992 had been adopted by seven lead refineries (22). The technology consists of a three-stage process in which the silver-rich crust is first liquated to reduce its lead content, then placed in a sealed furnace where the zinc is removed by vacuum distillation and, finally, the silver–lead metal is treated in a bottom blown oxygen cupel (BBOC) to produce a litharge slag and doré metal.

Liquation.   The rich crust is transferred to a cast-iron kettle installed in a refractory-lined furnace. The kettle is first filled with lead, which is melted by burners firing at both the top and bottom of the furnace. Firing is then continued only in the top zone to maintain a temperature of 720°C. The bath is covered with an eutectic sodium chloride–calcium chloride flux to minimize oxidation of zinc. Borax-based fluxes may also be used as cover.

Blocks of rich crust are added periodically and allowed to melt. As melting takes place, the lead-rich phase sinks to the bottom and is withdrawn from the kettle by a syphon. The lighter silver–zinc phase rises and floats on the surface of the lead. After sufficient silver–zinc alloy has accumulated, it is tapped from the top section of the kettle. In this manner it is possible to achieve a 120:1 concentration of the silver in the crust which is passed on for retorting. The lead removed from the bottom of the kettle typically contains 0.5% silver and 2% zinc.

Slags are also removed from the liquation kettle periodically. When chloride slags are formed these are cast into chunks and transferred to a wet plant for leaching to remove chlorides and treatment of the metallic residue. If borax slags are employed, metal values in the slag are recovered by further pyrometallurgical treatment.

Typically, for every ton of Parkes crust charged to a liquation kettle, about 0.25 t of triple alloy and 0.1 t of slag are generated. The triple alloy generally contains 30% silver, 10% lead, and 60% zinc.

Vacuum Retorting.   Classical Faber du Faur retorting of the triple alloy, in which small charges of crust are heated in clay graphite crucibles, has inherent disadvantages: low zinc recovery, high labor requirements because of the need to use multiple furnaces, and hot and arduous working conditions. A process whereby the crust was heated under vacuum in a refractory-lined vessel was developed by Pennaroya. The bath of this process is quiescent, however, and the distillation rate of the zinc is low owing to only convectional agitation of the charge. During the 1970s Metallurgie Hoboken Overpelt in conjunction with Otto Junker developed a new process in which the charge is heated under

vacuum using electric induction coils. The turbulence created in the bath by the induction currents results in a much higher distillation rate.

In practice, triple alloy is added to a clay graphite crucible in a refractory-lined vacuum-tight chamber (Fig. 12). Power input is controlled by adjusting the applied voltage until the charge is melted. A refractory cover is placed over the crucible and sealed with sand. The furnace cover contains an opening which mates with a port connecting to a condenser.

The process operates at 1 kPa (10 mbars) and 450 kW of power. When the condenser temperature reaches 580°C, the power is reduced to 350 kW. Cooling water is applied to the condenser, throughout distillation, by means of sprays. Normally distillation takes 10–12 hours and the end point is signified by an increase in furnace temperature and a decrease in vapor temperature to 500–520°C. At this point the power is turned off and the vacuum pump is shut down. Nitrogen is then bled into the system to prevent oxidation of zinc.

The taphole of the condenser is then opened and the molten zinc released is cast into molds. The zinc is returned to the refinery for reuse in the desilverizing process. After the vacuum furnace is disconnected from the condenser, it is tilted to pour the residual retort bullion in molds. The zinc content of the bullion is <3%. The residual bullion contains about 96% of the silver and 80% of the lead charged to the vacuum furnace. The balance of these elements is distributed between the distilled zinc metal and a retort slag. Vacuum retorting raises the silver content of the bullion from 30 to 75%, with lead essentially making up the balance.

Cupellation.   The final stage in the recovery of silver (and gold) is the cupellation of the retort bullion. Until the 1980s this was carried out in small reverberatory furnaces (cupels) fired by oil and gas burners, in which air was blown across the surface of the bath through tuyeres. The furnace was periodically tilted to allow lead oxide (litharge) to flow out. This process suffers from several disadvantages: formation of zinc dross when the bullion is initially melted, high (8%) silver losses to the skimmed litharge, low fuel efficiency, and poor reaction rates between the oxygen in the tuyere air and lead in the bath.

These deficiencies were overcome with the development of the bottom blown oxygen cupel (BBOC), a refractory-lined cylindrical furnace having a hydraulically tilted mechanism (Fig. 13). The furnace is top fired using a natural gas–air burner and is also top charged. The key feature is the consumable lance through which oxygen is blown to convert lead to lead oxide. The lance is also shrouded with nitrogen, and as it is worn down it is automatically advanced to maintain a constant position in the furnace. The design of the furnace allows for tilting to the optimum positions for both blowing and slag removal. Oxygen is virtually totally absorbed and there is little turbulence on the charge surface.

In practice, blocks of vacuum retort bullion are added to the furnace while in the vertical position and melted by the natural gas–air burner. The furnace is tilted (Fig. 13**a**) and blowing commenced. The burner is turned off, but blowing is continued. The zinc in the charge is oxidized first to form a viscous slag, but as blowing continues the litharge formed dilutes the zinc content and a fluid slag is formed. After one and a half hours the furnace temperature is stabilized at about 900°C and the first slag can be tapped. The furnace is tilted (Fig. 13**b**) and slag is poured into molds.

Oxygen blowing is continued to remove the remainder of the lead and the burner is used on low fire because the heat of reaction is not sufficient as the lead content of the bullion decreases. Litharge is again tapped and the process continued until the silver concentration exceeds 99.0%. At this point residual copper is removed by the addition of ingots of lead. The bath is maintained at a temperature of 960°C while sufficient lead is added and converted to lead oxide, which in turn carries copper oxide with it into the litharge slag. It is possible to reduce copper levels in the silver to <0.04% by this method. When the copper content is reduced to the desired level, the oxygen is turned off and the bath purged with nitrogen from the lance to reduce the oxygen content of the silver. The furnace is then tilted to the pouring position and the silver is cast into molds. Using the BBOC it is possible to recover 97% of the silver in the charge as doré metal. The balance of the silver is in the litharge, and is recovered by recycling the litharge to the softening operation.

Bismuth concentrates in the doré until the last stages of cupellation, when it is oxidized and removed with the litharge. After the last litharge has been removed, it is often necessary to add bars of refined lead to provide more litharge to carry off the last traces of bismuth. The doré metal is then cast into bars for marketing.

The good litharge is used as the oxidizer in batch reverberatory/kettle softening, and the other by-products, such as excess good litharge, coppery litharge, and niter skims and fume, are transferred to the smelting departments for recovery of the metal content.

Dezincing. The lead from the desilverizing contains 0.5–0.6% zinc which must be removed to meet standard specifications. This may be accomplished by vacuum distillation, or oxidation using caustic soda, ie, the Harris process.

The advantage of vacuum dezincing of desilverized bullion is that over 90% of the zic is recovered as metallic zinc. The equipment consists of a steel kettle of suitable capacity and a water-cooled condenser unit which sits over the lead bath and mates with the kettle to make a vacuum-tight enclosure. A vacuum is maintained inside the dezincing chamber which is equipped with a water-cooled condensing pan extending over the top of the chamber. The molten lead is agitated by an impeller.

The dezincing chamber is set first in the drossed lead bath, then water connections are immediately made in order to prevent the formation of steam within the water jacket. While the temperature is being raised, the vacuum pump is placed in operation and the agitator started. The temperature is then raised to 600°C and held throughout the operation.

After several hours, depending on the size of the unit, the vacuum is broken and the dezincing condenser unit is lifted from the bath. The metallic zinc condenses during the operation into a coherent crystalline mass and adheres to the underside of the water-cooled condenser. It is removed from each charge by manually applying a steel rake to dislodge the zinc deposit. The zinc drops off into suitable containers and is used again in the desilverizing process.

Bismuth Removal. When the bismuth level is >0.05%, it is removed from the lead to meet commercial specifications and bismuth is recovered as a product (24,25). The procedure takes advantage of the extremely low solubility of an intermetallic compound, $CaMg_2Bi_2$, that is formed between the reagents

and the impurity. The bismuth content can be reduced to <0.005% (see BISMUTH AND BISMUTH ALLOYS).

In the Betterton-Kroll process the dezinced lead is pumped to the debismuthizing kettle, in which special care is taken to remove drosses that wastefully consume the calcium and magnesium. The skimmed blocks from the previous debismuthizing kettle are added to the bath at 420°C and stirred for a short time to enrich the dross with the bismuth being extracted from the new charge. This enriched dross is skimmed to blocks and sent to the bismuth recovery plant.

Following the removal of the enriched dross, the required quantities of calcium, as a lead–calcium alloy and magnesium in the form of metal ingots, are added. The bath is stirred about 30 min to incorporate the reagents and hasten the reaction. The molten lead is cooled gradually to 380°C to permit the precipitate to grow and solidify. The dross is skimmed for use with the next lot of lead to be treated.

The lead contains residual calcium and magnesium that must be removed by chlorination or treatment with caustic and niter. The molten lead is pumped or laundered to the casting kettles in which it is again treated with caustic and niter prior to molding. After a final drossing, the refined lead is cast into 45-kg pigs or 1- and 2-t blocks.

Electrolytic Refining. Electrolytic refining (26,27), removes impurities in one step as slimes. The impurities must then be separated and purified. Before the development of the Betterton-Kroll process, electrolytic refining was the only practical method of reducing bismuth to the required concentrations.

Decopperized blast furnace bullion is softened to reduce impurities below 2% before casting as anodes. The electrolyte is a solution of lead fluosilicate [25808-74-6], $PbSiF_6$, and free fluosilicic acid [16961-83-4]. Cathode starting sheets are made from pure electrolytic lead. The concrete electrolytic cells are lined with asphalt or a plastic material such as polyethylene.

The electrolyte is prepared by dipping granulated lead, suspended in a basket, into and out of the fluosilicic acid. The lead oxidizes during the operation and lead fluosilicate is formed:

$$2\,H_2SiF_6 + 2\,Pb + O_2 \longrightarrow 2\,PbSiF_6 + 2\,H_2O$$
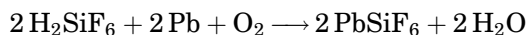
A typical electrolyte has a spcific gravity of 1.21 and the following analysis: lead, 67 g/L; free H_2SiF_6, 95 g/L; total acid, 142 g/L. The addition reagents added to the electrolyte are a comination of glue with either Goulac or Binderine (1 kg/t of Pb).

The temperature in the cell is 40°C. Most electrolyte cells are equipped with 24 anodes spaced approximately 10 cm apart, center to center; 25 cathode starting sheets are used, one at each end and others evenly spaced between the anodes. Current density is typically 15 mA/cm^2 of cathode area; cell voltage ranges from 0.30 to 0.70 V, and a current efficiency of 90−95% is usually realized.

The deposition time should be limited to a four-day period to avoid increased weight and roughness of the deposit. Deposited cathodes, weighing approximately 70 kg each, are thoroughly washed by dipping or by a high

pressure water spray. These are charged to large melting kettles, heated to ca 550°C, drossed, and cast into ingots.

Slimes Treatment. After the corroded anodes are washed, and the adhering slimes scraped off, filtered, and dried, approximately 8% moisture is left to prevent dusting. The general practice is to smelt the slimes in a small reverberatory furnace, which produces a slag 10–12% by weight of the slimes. This slag is taken to a second small reverberatory furnace in which it is partially reduced to remove precious metals; the remainder is transferred to the smelting department for production of antimonial lead. The reduced portion, containing the precious metals, is returned to the original slimes-smelting furnace. By antimony is fumed off to either a baghouse or a Cottrell unit.

The metal bath containing gold, silver, bismuth, copper, etc, together with the lead and antimony remaining after blowing, is transferred to a cupel furnace. The surface of the bath is blown by low pressure air, and the antimony in the bath is removed in a lead–antimony slag. As succeeding stages of oxidation take place, litharge containing increasing amounts of copper and bismuth is removed until the metal arrives at the doré stage and the bath has the appearance of metallic silver. If selenium and tellurium are present, niter is added to the bath and, by agitation and oxidation, the sodium salts of selenium and tellurium are formed and skimmed from the furnace. Upon completion of the cupellation stage the fineness of the doré is 996, ie, 996 parts gold plus silver per thousand parts metal. The doré metal is cast into suitable shapes for parting (separating gold from silver), followed by electrolytic refining of gold and silver.

Slag and litharge formed during cupellation are segregated and reduced to a metal containing 20–25% ore more bismuth, depending on the bismuth content of the original bullion, and transferred to a bismuth recovery plant.

5.5. Secondary Lead. The emphasis in technological development for the lead industry is on secondary or recycled lead. Recovery from scrap is an important source for the lead demands of the United States and the rest of the world. In the United States, over 81% of the lead requirements are satisfied by recycled lead products. The ratio of secondary to primary lead increases with increasing lead consumption for batteries. Well-organized collecting channels are required for a stable future for lead (see BATTERIES, OTHER SECONDARY CELLS; RECYCLING, NONFERROUS METALS).

The principal types of scrap are battery plates and paste, drosses, skimmings, and industrial scrap such as solders, babbitts, cable sheathing, etc. Some of this material is reclaimed by kettle melting and refining. However, most scrap is a combination of metallic lead and its alloying constituents mixed with compounds of these metals, usually oxides and sulfates. Therefore, recovery as metals requires reduction and refining procedures.

Because about 83% of the lead consumed in the United States is for use in lead–acid batteries, most recycled lead derives from this source of scrap. About 97% of the lead is reclaimed. Hence, the bulk of the recycling industry is centered on the processing of lead battery scrap.

The lead-bearing components are released from the case and other nonlead-containing parts, followed by the smelting of the battery plates, and refinement to pure lead or specification alloys. The trend toward battery grid alloys having little or no antimony, increases the ability of a recovery process to produce soft

lead (refined). As required in the production of primary lead, each step in the sec-ondary operations must meet the environmental standards for lead concentra-tion in air (see AIR POLLUTION; LEAD COMPOUNDS, INDUSTRIAL TOXICOLOGY).

A typical automobile battery weighs 16.4 kg and consists of 3.5 kg metallic lead, 2.6 kg lead oxides, 4.0 kg lead sulfate, 1.3 kg polypropylene, 1.1 kg PVC, rubber and other separators, and 3.9 kg electrolyte. Including acid and water, the lead-bearing parts represent 61 wt%, ie, 21 wt% of lead alloy (2% Sb) and 40 wt% lead oxides and sulfate. Nonlead-bearing parts constitute the remaining 39%: the case (hard rubber or polypropylene) and separators (PVC) at 15 wt% and the electrolyte at 24 wt%.

Battery Breaking.   There are well-defined, sophisticated technologies for the recovery of all materials of value in a battery (28). Technologies developed by Engitec (Milan, Italy) and M.A. Industries (Atlanta, Georgia) are generally employed. Figure 14 shows the flow sheet for a typical battery breaking system.

Battery breaking technologies use wet classification to separate the compo-nents of crushed batteries. Before crushing, the sulfuric acid is drained from the batteries. The sulfuric acid is collected and stored for use at a later stage in the process, or it may be upgraded by a solvent extraction process for reuse in battery acid.

After acid removal, scrap batteries are fed to a hammer mill in which they are ground to ≤ 5 cm particles. The ground components are fed to a conveyor and passed by a magnet to remove undesirable contamination. The lead scrap is then classified on a wet screen through which fine particles of lead sulfate and lead oxide pass, and the large oversize solid particles are passed on to a hydrodynamic separator. The fine particles are settled to a thick slurry and the clarified wash water recirulated to the wet screen.

The large particles sent to the hydrodynamic separator consist of metallic lead from the grids and poles in the battery together with ebonite [12765-25-2] and plastics from the cases and cell separators. In the hydrodynamic separator the feed is divided into three fractions: polypropylene chips in the upper section, metallics in the lower section, and ebonite and separators in the middle. The polypropylene chips are floated off, the metallics conveyed from the bottom, and the ebonite and separators are carried through in the water to a screen for further separation. The polypropylene is available for recycling, very often as battery cases, and the metallic lead is transferred to furnaces or kettles for refining (see RECYCLING, PLASTICS).

The paste recovered in the initial screening stage is not in a form suitable for lead smelting because of its high sulfate content. Thus the first step is desul-furization by a soda ash treatment at $60-70°$C.

$$PbSO_4\,(s) + Na_2CO_3\,(aq) \longrightarrow PbCO_3\,(s) + Na_2SO_4\,(aq)$$
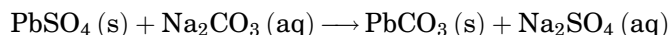
The products of reaction are pumped to a filter press for separation into a sodium sulfate solution and a filter cake having a low moisture content. The filter cake is then ready to be processed for the recovery of lead. The filtrate from the process contains an excess of sodium carbonate, and can be neutralized using the sulfuric acid drained from the batteries.

$$Na_2CO_3 + H_2SO_4 \longrightarrow Na_2SO_4 + H_2O + CO_2$$
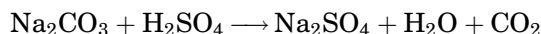
The sodium sulfate solution may be discharged or futher treated to recover sodium sulfate crystals or converted to other sodium salts for sale.

Almost all battery scrap and paste is converted to impure lead or lead alloys by pyrometallurgical processes employing blast, reverberatory, rotary, Isamelt, or electric furnaces. In many plants, a furnace combination is used. Electrowinning technologies have also been developed but as of this writing none is yet in full commercial operation.

Smelting. Blast Furnace. If whole battery scrap is the feed, a blast furnace must be used (29). The furnace is constructed similarly to the cupola employed in the foundry industry (see Copper alloys). The melting zone is water jacketed and the shaft above is refractory lined. A normal charge consists of lead-bearing materials, ie, battery plates, drosses, slags, and lead scrap; and limestone, coke, silica, and scrap iron. The scrap iron is added to combine with the sulfur which is present as sulfate in the filler, forming an iron matte high (5−15%) in lead and usually discarded.

Use of a blast furnace is preferred if a regular supply of a charge of coarse and consistent quality is available. However, the blast furnace is not suitable for treating finely divided feed material.

Reverberatory Furnace. Using a reverberatory furnace, a fine particle feed can be used, the antimony content can be controlled, and batch operations can be carried out when the supply of scrap material is limited. However, the antimony-rich slags formed must be reduced in a blast furnace to recover the contained antimony and lead. For treating battery scrap, the reverberatory furnace serves as a large melting facility where the metallic components are liquefied and the oxides and sulfate in the filler material are concurrently reduced to lead metal and the antimony is oxidized. The furnace products are antimony-rich (5 to 9%) slag and low antimony (less than 1%) lead.

The overall recovery of the metallic components of scrap in plants having both reverberatory and blast furnaces is over 95%.

Rotary Furnace. The rotary furnace, which has more flexibility than either the blast or reverberatory furnace, can produce either a single metal product or a high and a low antimonial alloy. The rotary furnace, like the reverberatory furnace, allows for the option of producing low antimony lead for further refinement.

However, rotary furnaces tend to produce more exhaust gas and fumes, require more skillful manipulation, and are more labor intensive. Also, the slags produced in the rotary furnaces, soda or fayalite [13918-37-1] slags, normally do not pass the toxic characteristic leach procedure (TCLP) test and pose a disposal problem.

Electric Furnace for Secondary Slags. The slag from the reverberatory furnace is treated in a submerged arc electric furnace (30). Slag, reducing agents, and fluxes are blended. The mixed charge is fed to the furnace via a steel pan conveyor which discharges the blended slag charge to a rotary dryer fired by the hot off-gases from the electric furnace. The slag is dried and heated prior to charging into the furnace. In the electric furnace, Sb, As, and Sn are reduced from the slag. The CO from the reduction process is burned as it exits the furnace

to provide heat for the dryer. The furnace is operated on a batch basis. When the furnace is fully charged (about 30 t of slag) the slag is held at constant temperature for a period of time to reduce the metal content to the desired level and produce a nonhazardous throwaway slag. The typical slag composition in wt% is CaO, 25–34; SiO_2, 22–35; FeO, 10–23; S, 1–3; Pb,<2; Sb, <1.5; Sn, <1.5; and As, <0.5.

The slag is batch tapped into a receiving room where it is cooled and broken up for disposal. The metal bullion is tapped from the furnace periodically via a siphon into 2-t cast-iron molds. Typical bullion content from an electric furnace in wt% is Sb, 13–18; Sn, 1–2; As, 0.5–1; Cu, 0.3–0.4; and Ni, 0.05–0.1. The balance is lead.

Gases from the furnace, metal tap, and feed system are combined and fed to a six-cell pulse baghouse containing 864 high temperature Teflon bags. The dust from the electric furnance system is fed continuously back to the reverberatory furnace in a close screw conveyor.

Isasmelt Furnace.   The Isasmelt furnace, originally developed for the production of primary lead, has also been adapted to treat desulfurized or non-desulfurized paste, to produce an impure bullion and a litharge slag. The slag is reduced in a rotary furnace to produce bullion and a discard slag. Also, the grid and plates produced during the battery breaking operation can be melted in an Isasmelt furnace to produce hard lead (31).

Other Developments.   A process (28) for the production of electrolytic lead from battery paste was developed. The desulfurized paste is leached using a solution of fluoboric acid and lead fluoborate, ie, spent electrolyte from lead electrowining. Hydrogen peroxide is used to convert Pb^{4+} to Pb^{2+}. The lead solution is treated by electrowinning in cascade cells using a specially designed proprietary composite anode.

The cathode material is stainless steel. The lead produced by this method analyzes 99.99+%. The overall power consumption is less than 1 kWh/kg of lead, so that the electrolytic process for treating spent batteries has much less of an environmental impact than the conventional pyrometallurgical process.

In another development (32), the sodium sulfate solution produced during the desulfurization of paste with caustic soda is electrolyzed in a membrane cell to produce caustic soda and high purity sulfuric acid. The caustic soda is recycled to the desulfurization stage; the sulfuric acid, after concentration, can be reused in battery production.

A similar development, is an environmentally clean process (33) to recover high purity lead as electrowon cathode. The process consists of decomposing the desulfurized paste to PbO at 325°C and leaching the PbO with fluosilcic acid, ie, spent electrolyte from electrowinning, to produce the soluble $PbSiF_6$. Lead is electrowon from the leach solution using a PbO_2-coated graphite anode. The cathode material is sheet lead. The purity of lead exceeds 99.99%. The power cosumption for electrowining is expected to be 660 kWh/t.

The electrowinning process developed by Ginatta (34) is available for licensing (qv). A process to upgrade the polypropylene chips from the battery breaking operation to pellets for use by the plastics industry. A solvent-extraction process has been developed to purify the spent acid from lead-acid batteries and use the purified acid in battery production has been reported (35).

6. Economic Aspects

Estimated world use of lead rose between 2% and 3% in 2004. China's use of lead in vehicle fleet expansion, production of automotive batteries for export, and investment in telecommunications and information technology was the main driving force for the increase. Europe's lead use increased by 1.5%. Refined lead production was nearly stagnant in 2004 and a production deficit is expected to continue.

United States mine production decreased by 5% in 2004. Production of secondary refined lead, mostly from spent lead-acid batteries, increased by 3.5% and the U.S. reported an increase in lead consumption of about 2%. Early in 2004 there was a significant increase in shipments of original materials and replacement SLI batteries. During the period 1997-2001 the lead-acid battery industry recycled more than 97% of the available lead scrap. This recycling rate ranked higher than that of any other recyclable material.

During 2004, the price of refined lead increased in the U.S. and world markets. The average North American price was ca $0.53/lb and the London Metal Exchange price was ca $0.39.lb.

Table 6 gives U.S. economic statistics for the period 2000-2004 (1).

7. Analytical Methods

Lead is detected qualitatively in solution by the formation of inorganic precipitates between lead and the following reagents: sulfuric acid or a soluble sulfate, giving a white precipitate; hydrochloric acid or a soluble chloride, giving a white crystalline precipitate; a soluble iodide, chromate, or dichromate, giving a yellow precipitate. Lead may also be detected upon formation of precipitates with many organic reagents such an oxalate and tannic acid. Macro amounts of lead are determined quantitatively by gravimetric methods, by weighing the lead as one of the above mentioned precipitates, or by electrolytic deposition on the anode as lead dioxides. There are also numerous titrimetric methods for determining macro amounts of lead quantitatively, mainly titration with molybdate or EDTA.

In determining the purity or percentage of lead in lead and lead-base alloys, the impurities or minor components are determined and the lead content calculated by difference. Quality control in lead production requires that the concentration of impurities meet standard ASTM specifications B29 (see Table 7). Analyses of the individual impurities are performed using various wet chemical procedures and instrumental methods such as emission spectroscopy.

8. Health and Safety Factors

8.1. Exposure. Exposure to lead can occur from a variety of occupational or nonoccupational sources. A comprehensive treatise on human lead exposure is available (36).

Nonoccupational. Lead enters the biosphere both through natural and human (anthropogenic) activities. Lead enters the atmosphere from natural occurrences such as erosion of the earth's crust, volcanic eruptions and emissions, and forest fires. The main source of atmospheric lead, however, is from anthropogenic lead emissions. Combustion of petroleum (qv) and its derivatives, especially leaded gasoline, accounts for the majority of atmospheric lead worldwide (37). The greatest increase in global emissions started in the 1920s when lead began to be used as an additive in gasoline (38) (see GASOLINE AND OTHER MOTOR FUELS). Because of human health concerns, the use of leaded gasoline has declined sharply especially in the United States. Production of lead, zinc, copper(qv), iron(qv), and steel(qv) also contributes significantly to atmospheric lead, and a wide range of lead concentrations in air have been reported (4). Most urban areas in the United States have air lead concentrations of <0.5 $\mu g/m^3$ on average (5) (see also AIR POLLUTION).

Lead is a natural constituent of soils, ranging from 10 to 50 $\mu g/g$ in uncontaminated areas. Urban soils, however, may contain lead from a variety of sources including automobile exhaust, industrial activity, and deteriorating or intentionally removed leaded paint. The lead content of roadside soils has been found to be as high as 2000 $\mu g/g$ within two meters of the curb (37). These levels generally decline exponentially to background levels within 10−25 meters of the curb. Within three meters of houses coated with lead-based paints, soil lead concentrations may exceed 1000 $\mu g/g$. Exposure to soil lead may occur from vegetable consumption and by direct or indirect ingestion of soils or soil dust, particularly by children.

Lead is present in trace amounts in surface and ground waters. Because lead forms insoluble salts or is sorbed onto sediment particles, atmospheric lead deposition or surface runoff generally does not affect overall lead concentration. Most natural waters are low (<5 $\mu g/L$) in lead content (37). Drinking water (qv), however, can contain markedly higher lead concentrations owing to contact with lead-bearing pipes, solder, and plumbing fixtures. Waters that are relatively acidic or soft may contain elevated lead levels at the tap (37), and often represent a principal source of lead exposure. In the United States, the maximum contaminant level for lead in drinking water is 15 $\mu g/L$. The use of lead solder for materials contacting residential water supplies was banned in the United States in accordance to the 1986 Amendments to the Safe Drinking Water Act.

Ingestion of foods represents the majority of the daily intake of lead for most people, although this is not the route responsible for marked elevations of an individual's lead burden (37,38). The lead content of food can be attributed to such factors as foliar uptake of atmospheric lead by plants; contamination during harvesting and processing; use of water containing lead during food processing (qv) or preparation; lead solder in food cans; lead fallout from urban dusts in the kitchen; and the use of lead-containing glazes in pottery. The awareness of these causes for lead contamination of foods, and subsequent regulatory and voluntary actions, have resulted in a marked reduction in the lead in foods, from pre-1975 values of >250 $\mu g/d$ to ≤ 50 $\mu g/d$ in 1993 (37).

Occupational. The toxicity of lead following occupational exposure to the metal has been known since antiquity. In developed countries, regulations,

engineering advances, and medical surveillance have greatly reduced the incidence of clinical lead poisoning in lead-based industries (39). The occupational lead poisoning, defined as a whole blood lead concentration > 50 µg/dL (40), continues to be a problem, however (6,7), and severe exposures to lead continue to occur in workers in a variety of manufacturing processes (5–7). Lead smelting and refining have the greatest potential for occupational exposure to inorganic lead, because lead fumes are generated and dust containing lead oxide is deposited in the workplace. Other occupations associated with lead exposure include lead storage battery manufacture; autobody and auto radiator manufacture and repair; lead recycling; stained glass work; leaded paint removal; welding (qv); demolition and restoration; and plumbing installation or repair. More detailed listings of occupations and occupational settings with potential for lead exposure are available (39,40). The U.S. National Institute for Occupational Safety and Health (NIOSH) has published guidelines for minimizing occupational exposure to lead (7). At a minimum, airborne lead concentrations in the workplace should not exceed the Occupational Safety and Health Administration's (OSHA) permissible exposure level (PEL) of 50 µg/m^3.

Elevated blood lead levels have occurred in children of workers who are occupationally exposed to lead (38,39). Because children may be exposed to lead dust brought home on workers' clothing, in the United States the OSHA lead standard requires employers in traditional lead-related occupations to provide showers, changing facilities, and laundered work clothes. Moreover, workers must shower and change out of work clothes before leaving the workplace. However, these and other OSHA lead standards do not apply to workers in the less traditional lead-related occupations such as construction, plumbing, painting, demolition, and restoration.

8.2. Toxicity.   Reviews on the occurrence, biochemical basis, and treatment of lead toxicity in children (41) and workers (36,42,43) have been published. Public health surveillance data document that each year thousands of American workers occupationally exposed to lead develop signs and symptoms indicative of lead poisoning (36).

Lead is toxic to the kidney, cardiovascular system, developing red blood cells, and the nervous system. The toxicity of lead to the kidney is manifested by chronic nephropathy and appears to result from long-term, relatively high dose exposure to lead. It appears that the toxicity of lead to the kidney results from effects on the cells lining the proximal tubules. Lead inhibits the metabolic activation of vitamin D in these cells, and induces the formation of dense lead–protein complexes, causing a progressive destruction of the proximal tubules (43). Lead has been implicated in causing hypertension as a result of a direct action on vascular smooth muscle as well as the toxic effects on the kidneys (42,43).

Lead-induced anemia results from impairment of heme biosynthesis and acceleration of red blood cell destruction (43). Lead-induced inhibition of heme biosynthesis is caused by inhibition of 5-aminolevulinic acid dehydratase and ferrochelatase which starts to occur at blood lead levels of 10 to 20 µg/dL and 25 to 30 µg/dL, respectively (43). Anemia, however, is not manifested until higher levels are reached.

In the peripheral nervous system, motor axons are the principal target. Lead-induced pathological changes in these fibers include segmental demyelination and axonal degeneration (43). Extensor muscle palsy with wrist drop or ankle drop is the classic clinical manifestation of this toxicity. Lead-induced central nervous system toxicity, or lead encephalopathy, is the most serious manifestation of lead toxicity. It is more common in children than in adults. The toxicity is believed to arise from demyelination and nerve degeneration. Early signs of lead encephalopathy include clumsiness, vertigo, ataxia, falling, headaches, insomnia, restlessness, and irritability. If untreated, delerium, tonic—clonic convulsions, mental retardation, and even death may ensue (38,43).

Lead is known to cause reproductive and developmental toxicity. Decreased sperm counts and abnormal sperm development have been reported in male workers heavily exposed to lead. Increased incidences of spontaneous abortion have been reported in female lead workers as well as in the wives of male lead workers (43). Lead crosses the placenta and has been found to cause irreversible neurologic impairment to the fetus at maternal blood levels as low as 15 to 20 μg/dL (43).

The American Conference of Governmental Industrial Hygienists (ACGIH) threshold limit value (TLV) for inorganic lead (fumes and dust) is 0.05 mg/m^3. The TLV for lead arsenate ($PbHAsO_4$) is 0.15 mg/m^3. Lead chromate is classified as an A_2 carcinogen (suspected human carcinogen) by the ACGIH, and the TLV is 0.05 mg/m^3 of lead chromate as lead (44).

Lead in drinking water has been regulated in the United States to achieve a maximum contaminant level goal (MCLG) of zero and an action level of 15 μg/L (see GROUNDWATER MONITORING). No standards have been established for lead in soil, but 500—1000 ppm is generally accepted as a level not leading to elevated blood lead levels in young children. The Center for Disease Control (CDC) has selected 10 μg/dL of lead in blood as the upper area above which risk to young children is indicated. Follow-up samples are recommended when blood lead levels exceed 10 μg/dL.

Lead-based paint in old structures has been identified as an environmental risk because the chemical form of lead in paint is readily available biologically. Lead in paint is measured using a surface analysis of walls, windowsills, etc, using x-ray fluorescence spectrometry. The following criteria have been established by the United States CDC for lead in surficial materials: <0.07 mg/cm^3, negative; 0.7—2.9 mg/cm^3 low; 3.0—5.9 mg/cm^3 moderate; and ≥6.0 mg/cm^3 high.

Another level of regulatory significance is the toxic characteristic leach procedure (TCLP) limit of a characteristic waste. A material which is a waste because of the TCLP is hazardous if a liquor resulting from an 18-h leach in an acetic acid buffer exceeds 5 ppm (mg/L) lead in the leach liquor.

During 2002, United States government agencies issued new rules affecting the lead industry. The new rules include revision of regulations on the use of lead-containing chemicals in aerosol spray paints, in metal-cored candlewicks, and approval of a new nonlead ammunition, Television and computer components have been reclassified so as to effectively remove them as solid waste in certain regions of the U.S. (45).

9. Uses

The lead-acid industry continued to be the principal user of lead. It accounted for 83% of the U.S. reported consumption of lead. Lead-acid batteries were primarily used as starting-lighting-ignition (SLI) batteries for automobiles and trucks. These batteries are also used as industrial-type batteries for uninterruptible power sources for hospitals and communications and computer equipment; for load leveling equipment for commercial electrical power systems; and as traction batteries used in airline ground equipment, industrial forklifts, mining vehicles, and golf carts. About 11% of lead was used in ammunition; casting materials; sheets (including radiation shielding), pipes, traps and extruded products; cable covering, calking lead, and building construction; solder; and oxides for glass ceramics, pigments, and chemicals. The balance was used in ballast and counter weights, brass and broze, foil, terne metal, type metal, and wire.

Table 8 gives U.S. consumption of lead for the period 2001–2002 (45).

10. Lead Alloys

Lead has excellent resistance to corrosion in a wide variety of media, and is easily alloyed with many other metals. Lead alloys, which have low melting points, can be cast into many shapes by using a variety of molding materials and casting processes.

About 50% of lead is used as pure lead, lead oxides, or lead chemicals (see LEAD COMPOUNDS, INDUSTRIAL TOXICOLOGY); the remainder is used in the form of lead alloys. The principal uses of lead alloys are in lead–acid batteries (qv); for ammunition; cable sheathing; building construction in sheets, pipes, and solders; bearings; gaskets; specialty castings; anodes; fusible alloys; shielding; and weights (see BUILDING MATERIALS, SURVEY; BEARING MATERIALS; METAL ANODES; SOLDERS AND BRAZING FILLER METALS).

Lead and its alloys are generally melted, handled, and refined in cast-iron, cast-steel, welded-steel, or spun-steel melting kettles without fear of contamination by iron (qv). Normal melting procedures require no flux cover for lead. Special reactive metal alloys require special alloying elements, fluxes, or covers to prevent dross formation and loss of the alloying elements.

Lead is ductile and malleable, and can be fabricated into various shapes by rolling, extruding, forging, spinning, and hammering. The low tensile strength and very low creep strength of lead make it unsuitable for use without the addition of alloying elements. The principal alloying elements used to strengthen lead are antimony, calcium, tin, copper (qv), tellurium, arsenic, and silver. Minor alloying elements are selenium, sulfur, bismuth, cadmium, indium, aluminum, and strontium.

Lead and many of its alloys exhibit excellent corrosion resistance owing to the rapid formation of a passive, impermeable, insoluble protective film when the lead is exposed to the corrosive solution (see CORROSION AND CORROSION CONTROL).

Lead shows excellent resistance to phosphoric and sulfuric acid in almost all concentrations and at elevated temperatures, as well as to sulfide, sulfite,

and sulfate solutions. The corrosion film is insoluble lead sulfate which rapidly reforms if it is damaged. Lead is also resistant to chlorides, fluorides, and bromates at low concentrations and low temperatures. However, because lead is soluble in nitric and acetic acids, it is not resistant to these acids.

Because the corrosion resistance of lead and lead alloys is associated with the formation of the protective corrosion film, removal of the film in any way causes rapid attack. Thus the velocity of a solution passing over a surface can lead to significantly increased attack, particularly if the solution contains suspended particulate material. Lead is also attacked rapidly in the presence of high velocity deionized water. The lack of dissolved minerals in such water prevents the formation of an insoluble protective film. In most solutions, lead and lead alloys are resistant to galvanic corrosion because of the formation of a nonconductive corrosion film. In contact with more noble metals, however, lead can undergo galvanic attack which is accelerated by stray electrical currents.

The excellent corrosion-resistant lead dioxide, PbO_2, film formed on anodes and lead−acid battery positive grids in sulfuric acid has enabled lead insoluble anodes and lead−acid batteries to maintain the dominant positions in their respective fields.

10.1. Lead-Antimony Alloys. *Properties.* Lead−antimony alloys are the most widely used lead alloys. Antimony is relatively soluble in molten lead. The lead−antimony system contains a eutectic point at 11.1% antimony and 252°C. The solubility of antimony in solid lead decreases from 3.5 wt% at the eutectic temperature of 252°C to 0.25 wt% at 25°C. The reduced solubility with temperature makes the lead−antimony alloys age hardenable. The grain structure of a typical cast lead−antimony alloy is shown in Figure 15. It consists of a lead matrix (the dark particles in Fig. 15) surrounded by a network of antimony particles (white). These particles provide immediate strength upon casting and also provide high temperature strength. The addition of arsenic dramatically increases the rate of aging and final strength. Addition of tin increases the fluidity and, in combination with copper and arsenic, reduces the rate of oxidation of molten lead−antimony alloys (46).

The mechanical properties of lead−antimony alloys containing arsenic, tin, and copper are shown in Table 9. Most lead−antimony alloys of commercial importance contain 11 wt% or less antimony. High (>5 wt%) antimony alloys are strengthened primarily by the eutectic antimony particles produced during solidification of the alloy. Lower antimony alloys are strengthened by a combination of the eutectic particles and precipitation hardening during aging.

The decrease in solubility of antimony in lead with decreasing temperature allows the lead−antimony alloys to be precipitation-hardened by proper heat treatment. Differences in the rate of cooling of castings to room temperature can give wide variation in the mechanical properties owing to differences in the amount and type of antimony precipitates produced during cooling. The effects of quenching temperature on the properties of lead−3 wt% antimony alloy aged 1 day are as follows.

Quenching temperature, °C	Tensile strength, MPa (psi)
238	75 (10,875)
230	56 (8,120)
215	38 (5,510)
200	34 (4,930)

Uses. Lead–Acid Batteries. The primary use for lead–antimony alloys is as electrodes, connectors, and terminals of lead–acid batteries (see BATTERIES, ALKALINE SECONDARY CELLS). The lead–antimony alloys, which are strong, creep resistant, and corrosion resistant in sulfuric acid, resist structural changes caused by charge–discharge cycles in the battery. Antimony as an alloying element in the positive electrode grid aids in retaining the active material in the battery and also aids in recharge of the battery when it is deeply discharged. Deep discharge industrial, load-leveling, and motive-power batteries utilize lead alloys containing 5–11 wt% antimony. Large tubular grids use 9–11 wt% antimony.

In lead–acid batteries antimony has one disadvantage. In use, the positive lead grid is oxidized during battery charging. The antimony, oxidized from the positive grid, enters the electrolyte and plates on the negative grid as metallic antimony. The antimony reduces the hydrogen overvoltage at the negative grid causing breakdown of the water in the electrolyte during charging into hydrogen and oxygen, and consumes water in the process. The amount of water loss and subsequent need to add water to the battery decreases as the antimony content of the positive grid decreases (47). Low gassing or maintenance-free batteries have antimony contents of 1.5–2.75 wt%. At this level, the migration of antimony is greatly decreased.

Automobile battery grids employ about 1–3 wt% antimony–lead alloys. Hybrid batteries use low (1.6–2.5 wt%) alloys for the positive grids and non-antimony alloys for the negative grids to give reduced or no water loss. The posts and straps of virtually all lead–acid batteries are made of alloys containing about 3 wt% antimony.

Low antimony alloys decrease water loss when used as positive grids. In alloys having less than 3.5 wt% antimony, however, the increased solidification temperature range and the reduced or negligible amount of eutectic liquid present at the final freezing temperature produces structures highly susceptible to solidification–shrinkage porosity and cracking. The grain size of lead–antimony alloys increases with decreasing antimony content.

As the antimony content of the lead–antimony alloys decreases, the alloys tend to solidify into large, oriented, columnar grains. Figure 16**a** shows the large grains associated with a cast low antimony alloy battery grid. The large grains present areas for preferential mechanical cracking and penetrating corrosion. To prevent the formation of large grains, nucleants are added to lead–antimony alloys. Small amounts of sulfur, copper, or selenium serve as sites for growth of lead crystals during solidification and produce fine, rounded grain structures which are resistant to cracking (46,48–50).

By using nucleants, fine-grained structures, such as that shown in Figure 16**b**, can be produced in cast alloys independent of the antimony content. The molten metal must be kept at a temperature high enough to assure complete solubility of the nucleants prior to casting the alloy. In the United States primarily copper and sulfur are used as nucleants; in Europe and Asia selenium is used. At very low (1.0–1.6 wt%) antimony contents selenium is used exclusively.

Ammunition.   Lead shot is produced by dropping molten lead–antimony alloys containing 0.5–8 wt% antimony through holes in pans into water. The shot alloys contain arsenic in an amount equal to about 20–30 wt% of the antimony content. Arsenic permits the molten drop of lead to become round during freefall. Tin produces elongated shot if present, therefore it is restricted to less than 0.0005 wt%. Shot up to 5.8 mm in diameter is dropped from towers; larger shot must be cast in molds. Lead–antimony (0.5–3.0 wt%) alloys are also used for cast or swaged bullets. The U. S. Department of the interior issued a proposed Bill that would approve of given shot formulated without lead for hunting waterfowl (51).

Cable Sheathing.   Lead–antimony alloys containing 0.5–1.0 wt% antimony are used to form a barrier sheath in high voltage power cables. Lead–copper and lead–tin–arsenic alloys are also used. Antimony containing alloys are used when higher strength and resistance to vibration is required. British standard BS-801 alloy B contains 0.85 wt% antimony. Lead–antimony alloys having 0.6 wt% or less antimony can be continuously extruded, are impervious to oil and moisture, and remain pliable indefinitely. Lead–antimony (1.0 wt%) is generally used as sleeves for cable splices.

Anodes.   Lead–antimony (6–10 wt%) alloys containing 0.5–1.0 wt% arsenic have been used widely as anodes in copper, nickel, and chromium electrowinning and metal plating processes. Lead–antimony anodes have high strength and develop a corrosion-resistant protective layer of lead dioxide during use. Lead–antimony anodes are resistant to passivation when the current is frequently interrupted.

Wrought Lead–Antimony.   Most lead–antimony alloys are used in the cast form. Rolling, extruding, or drawing breaks up the ascast strengthening antimony eutectic particles, thus wrought lead–antimony alloys are weaker and have higher creep rates than cast lead–antimony alloys, but greater strength than lead–copper alloys. These can be easily fabricated into most lead products. Extruded and formed lead–4–6 wt% antimony alloys are used to produce a variety of products for radiation protection. Because of excellent resistance to corrosion by a variety of chemicals, lead–antimony (4–8 wt%) alloys are used for tank linings, pumps, valves, and heating and cooling coils, particularly where sulfuric acid or sulfate solutions are handled at elevated temperature. Arsenic is generally added to increase resistance to creep at elevated temperatures.

Lead–Antimony–Tin Alloys.   Lead–antimony–tin alloys are used for printing, bearings, solders, slush castings, and specialty castings. These alloys have low melting points, high hardness, and excellent high temperature strength and fluidity. Printing alloys generally contain more than 11 wt% antimony and 3–14 wt% tin. The alloys shown in Table 10 have low melting points and high

hardness for wear resistance in printing. Replication of mold details is particularly important.

Excellent antifriction properties and good hardness make lead–antimony–tin alloys suitable for journal bearings. The alloys contain 9–15 wt% antimony and 1–20 wt% tin and may also contain copper and arsenic, which improve compression, fatigue, and creep strength important in bearings. Lead–antimony–tin bearing alloys are listed in ASTM B23-92 (52).

Specialty castings include belt buckles, trophies, casket trim, miniature figures, and hollow-ware. Slush castings are produced by pouring an alloy into a mold, permitting a given thickness to solidify, and pouring out the remaining liquid to produce a hollow, light, high detail casting. The near-eutectic lead alloy, containing 11 wt% antimony, 1 wt% tin, and 0–0.5 wt% arsenic, has a low melting point which permits silicon rubber molds to be used in spin-casting processes. Lead–antimony–tin alloys for die casting are listed in ASTM B102-93 (52).

Low (2–5 wt%) antimony, low (2–5 wt%) tin lead alloys are used for automobile body solder. Special lead–antimony alloys containing 1–4 wt% antimony are used for wheel-balancing weights, battery cable clamps, collapsible tubes, and highly machined isotope pots.

10.2. Lead–Calcium Alloys. Lead–calcium alloys are replacing lead–antimony alloys for many applications. Most U.S. original equipment automotive batteries are constructed of lead–calcium grids, whereas most U.S. replacement batteries utilize lead–calcium alloys for the negative grid and lead–antimony alloys for the positive grid. Lead–calcium is used worldwide for standby power, submarine, and specialty sealed batteries. Lead–calcium alloy batteries do not require addition of water and can therefore be sealed. Lead–calcium alloys are used for electrowinning anodes, cable sheathing and sleeving, specialty boat keels, and lead alloy tapes.

Binary Lead–Calcium Alloys. The lead-calcium phase diagram is a peritectic having a peritectic temperature of 328.3°C. The maximum solubility of calcium is 0.10 wt% at 328.3°C and rapidly decreases to 0.02 wt% at 200°C and 0.01 wt% at 25°C. The large decrease in solubility with decreasing temperature permits precipitation strengthening of binary lead–calcium alloys by the compound Pb_3Ca. This compound is also formed in molten alloys containing more than 0.07% calcium.

Below 0.10 wt% calcium the alloys solidify into a cellular, dendritic grain structure as seen in Figure 17 (53). Impurities segregate to the intercellular boundaries and are thus accented in the microstructure. Reverse segregation causes some areas of the casting to contain 0.10 wt% calcium regardless of the original calcium content of the melt. Precipitation of calcium occurs by a discontinuous precipitation reaction (53). In this reaction, grain boundaries move through the matrix, the original cast grain is destroyed, and the characteristic serrated grain boundaries of lead–calcium alloys seen in Figure 18 are produced. The calcium content and the rate of grain boundary movement determine the final grain size and shape.

Lead–calcium (0.04%) alloy, used as cable sheaths and sleeves for cable splices, is significantly stronger and has greater creep resistance than lead–copper (0.06 wt%) or lead–antimony (1 wt%). Table 11 compares the mechanical

properties of lead–calcium alloy to these alloys and to pure lead. The lead–calcium alloys have outstanding creep and fatigue resistance as well as relatively good ductility. Aging after production may cause a permanent set and difficulty in uncoiling; hence, lead–calcium is used primarily in straight lengths or as sleeves.

The main use of binary lead–calcium alloys is for the grids in large, stationary standby power batteries. These batteries use alloys containing 0.03–0.07 wt% calcium. The alloy has sufficient strength for the application, but it is used principally because of its resistance of self-discharge and because it reduces water loss. The grids are large grained and resistant to growth and creep during the long battery life.

Reactivity of Lead–Calcium Alloys. Precise control of the calcium content is required to control the grain structure, corrosion resistance, and mechanical properties of lead–calcium alloys. Calcium reacts readily with air and other elements such as antimony, arsenic, and sulfur to produce oxides or intermetallic compounds (see CALCIUM AND CALCIUM ALLOYS). In these reactions, calcium is lost and suspended solids reduce fluidity and castibility. The very thin grids that are required for automotive batteries are difficult to cast from lead–calcium alloys.

A rapid method to determine the calcium content of lead alloys is a liquid-metal titration using lead–antimony (1%) (54). The end point is indicated by a gray oxide film pattern on the surface of a solidified sample of the metal when observed at a 45° angle to a light source. The basis for the titration is the reaction between calcium and antimony. The percentage of calcium in the sample can be calculated from the amount of antimony used. If additional calcium is needed in the alloy, the melt is sweetened with a lead–calcium (1 wt %) master alloy.

Lead–Calcium–Aluminum Alloys. Lead–calcium alloys can be protected against loss of calcium by addition of aluminum. Aluminum provides a protective oxide skin on molten lead–calcium alloys. Even when scrap is remelted, calcium content is maintained by the presence of 0.02 wt% aluminum. Alloys without aluminum rapidly lose calcium, whereas those that contain 0.03 wt% aluminum exhibit negligible calcium losses (55). Even with less than optimum aluminum levels, the rate of oxidation is lower than that of aluminum-free alloys.

Producing lead–calcium–aluminum alloys is difficult. Calcium and aluminum can be added simultaneously to lead using a calcium (73 wt%)–aluminum (27 wt%) master alloy (56) (see ALUMINUM AND ALUMINUM ALLOYS). Using this method, the calcium and aluminum contents can be precisely controlled. Pressed pellets of metallic aluminum and metallic calcium are also used.

Lead alloys containing 0.09–0.15 wt% calcium and 0.015–0.03 wt% aluminum are used for the negative battery grids of virtually all lead–acid batteries in the United States and are also used in Japan, Canada, and Europe. If the molten alloy is held at too low a temperature, the aluminum precipitates from solution, rises to the surface of the molten alloy as finely divided aluminum particles, and enters the dross layer atop the melt.

Lead–Calcium–Tin Alloys. Tin additions to lead–calcium and lead–calcium–aluminum alloys enhances the mechanical (53) and electrochemical properties (57). Tin additions reduce the rate of aging compared to lead–calcium

binary alloys. The positive grid alloys for maintenance-free lead–calcium batteries contain 0.3–1.2 wt% tin and also aluminum.

Cast lead–calcium–tin alloys usually contain 0.06–0.11 wt% calcium and 0.3 wt% tin. These have excellent fluidity, harden rapidly, have a fine grain structure, and are resistant to corrosion. Table 12 lists the mechanical properties of cast lead–calcium–tin alloys and other alloys.

Wrought lead–calcium–tin alloys contain more tin, have higher mechanical strength, exhibit greater stability, and are more creep resistant than the cast alloys. Rolled lead–calcium–tin alloy strip is used to produce automotive battery grids in a continuous process (58). Table 13 lists the mechanical properties of rolled lead–calcium–tin alloys, compared with lead–copper and rolled lead–antimony (6 wt%) alloys.

Lead Anodes. A principal use for lead–calcium–tin alloys is lead anodes for electrowinning. The lead–calcium anodes form a hard, adherent lead dioxide layer during use, resist corrosion, and greatly reduce lead contamination of the cathode. Anodes produced from cast lead–calcium (0.03–0.09 wt%) alloys have a tendency to warp owing to low mechanical strength and casting defects.

Wrought lead–calcium–tin anodes have replaced many cast lead–calcium anodes (59). Superior mechanical properties, uniform grain structure, low corrosion rates, and lack of casting defects result in increased life for wrought lead–calcium–tin anodes compared to other lead alloy anodes.

10.3. Lead–Copper Alloys. Copper is an alloying element as well as an impurity in lead. The lead–copper system has a eutectic point at 0.06% copper and 326°C. In lead refining, the copper content can thus be reduced to about 0.08% merely by cooling. Further refining requires chemical treatment. The solubility of copper in lead decreases to about 0.005% at 0°C.

High copper–lead alloys generally contain 60–70% copper. The mechanical properties of sand-cast copper–lead alloys are shown in Table 13. The high copper alloys are difficult to cast and are susceptible to extensive segregation. Cast lead–copper (60–70 wt%) alloys are used as bearing and bushings for high temperature service. More recently, the cast alloys have been replaced by sintered copper powder products infiltrated with lead to produce more uniform distribution of the lead.

Only lead alloys containing copper below 0.08% have practical applications. Lead sheet, pipe, cable sheathing, wire, and fabricated products are produced from lead–copper alloys having copper contents near the eutectic composition. Lead–copper alloys in the range 0.03–0.08 wt% copper are covered by many specifications: ASTM B29-92 (7), QQL 171 (United States), BS 334, HP2 Type 11 (Canada), DIN 1719 (Germany), and AS 1812 (Australia).

Lead–copper alloys are specified because of superior mechanical properties, creep resistance, corrosion resistance, and high temperature stability compared to pure lead. The mechanical properties of lead–copper alloys are compared to pure lead, and to lead–antimony and lead–calcium alloys in Tables 4 and 5.

Lead–copper alloys are the primary material used in the continuous extrusion of cable coverings for the electrical power cable industry in the United States. Other alloys, containing tin and arsenic as well as copper, have also been developed for cable sheathing in the United States to provide higher fatigue strength.

Extruded or rolled lead–copper alloys contain a uniform dispersion of copper particles in a lead matrix. Because the solid solubility of copper in lead is very low, copper particles in the matrix remain stable up to near the melting point of lead, maintaining uniform grain size even at elevated temperature.

Copper-containing lead alloys undergo less corrosion in sulfuric acid or sulfate solutions than pure lead or other lead alloys. The uniformly dispersed copper particles give rise to local cells in which lead forms the anode and copper forms the cathode. Through this anodic corrosion of the lead, an insoluble film of lead sulfate forms on the surface of the lead, passivating it and preventing further corrosion. The film, if damaged, rapidly reforms.

Lead–copper alloys are also used as tank linings, tubes for acid mist precipitators, steam heating pipes for sulfuric acid or chromate plating baths, and flashing and sheeting (see TANKS AND PRESSURE VESSELS).

10.4. Lead–Silver Alloys.   Silver readily forms alloys with lead. Lead is often used as a base metal solvent for silver recovery processes. The lead–silver system is a simple eutectic having the eutectic point at 2.5 wt% silver and 304°C. The solid solubility of silver in lead is 0.10 wt% at 304°C, dropping to less than 0.02 wt% at 20°C.

Lead–silver alloys show significant age hardening when quenched from elevated temperature. Because of the pronounced hardening which occurs using small amounts of silver, the content of silver as an impurity in pure lead is restricted to less than 0.0025 wt% in most specifications. Small additions of silver to lead produces high resistance to recrystallization and grain growth.

The principal uses for lead–silver alloys are as anodes and high temperature solders. Only lead–silver alloys containing less than 6 wt% silver are used commercially. Lead alloys containing 0.75–1.25 wt% silver are used as insoluble anodes in the electrowinning of zinc and manganese. Some zinc refineries have reduced the silver content of the anodes to as low as 0.25 wt%. Lead–calcium–silver anodes are also used for zinc electrowinning. Silver promotes the formation of very hard, dense, electrically conducting layers of lead dioxide on the surface of the anode.

Silver reduces the oxygen evolution potential at the anode, which reduces the rate of corrosion and decreases lead contamination of the cathode. Lead–antimony–silver alloy anodes are used for the production of thin copper foil for use in electronics. Lead–silver (2 wt%), lead–silver (1 wt%)–tin (1 wt%), and lead–antimony (6 wt%)–silver (1–2 wt%) alloys are used as anodes in cathodic protection of steel pipes and structures in fresh, brackish, or seawater. The lead dioxide layer is not only conductive, but also resists decomposition in chloride environments. Silver-free alloys rapidly become passivated and scale badly in seawater. Silver is also added to the positive grids of lead–acid batteries in small amounts (0.005–0.05 wt%) to reduce the rate of corrosion.

Lead–silver alloys are used extensively as soft solders; these contain 1–6 wt% silver. Lead–silver solders have a narrower freezing range and higher melting point (304°C) than conventional solders. Solders containing 2.5 wt% silver or less are used either as binary alloys or combined with 0.5–2 wt% tin. Lead–silver solders have excellent corrosion resistance. The composition of lead–silver solders is listed in ASTM B32-93 (solder alloys) (52).

10.5. Lead–Tellurium Alloys. Tellurium is often used in lead alloys when high mechanical strength at minimal alloy content is required. It is used for pipes and sheets, shielding for nuclear reactors (qv), and cable sheathing. Lead alloys containing 0.035–0.10 wt% tellurium generally also contain copper in amounts of 0.03–0.08 wt%. The U.S. Federal Specifications QQL-201F and ASTM B749-91 (7) cover the use of wrought lead–tellurium alloys. Lead–tellurium alloys for cable sheathing are specified by German DIN 17 640.

Cold-rolled alloys of lead with 0.06 wt% tellurium often attain ultimate tensile strengths of 25–30 MPa (3625–5350 psi). High mechanical strength, excellent creep resistance, and low levels of alloying elements have made lead–tellurium alloys the primary material for nuclear shielding for small reactors such as those aboard submarines. The alloy is self-supporting and does not generate secondary radiation.

Wrought or extruded lead–tellurium (0.035–0.10 wt%) alloys produce extremely fine grains. The binary alloy is, however, susceptible to recrystallization. The addition of copper or silver reduces grain growth and retains the fine grain size. Because tellurium is a poison for sealed lead–acid batteries, the tellurium content of lead and lead alloys used for such purposes is usually restricted to less than 1 ppm.

10.6. Lead–Tin Alloys. Lead alloys with tin in all proportions, providing a series of alloys that have wide application in many industries. The phase diagram shows a eutectic composition of 61.9 wt% Sn–39.1 wt% Pb melting at 183°C. The solid solution of tin in lead decreases from 19.0 wt% at 183°C to 1.9 wt% at 20°C, and the solubility of lead in tin ranges from 2.5 wt% at 183°C to <0.3 wt% at 20 °C.

Solders. The principal use of lead–tin alloys is as solders for sealing and joining metals. Solders range in composition from 20 to 98 wt% lead, the remainder being tin. Lead–tin (2 wt%) solder is used to seal the side seams of steel (tin) cans. Additions of 0.5 wt% silver to the alloy significantly improves the creep strength which is essential in pressurized cans. Pre-tinned cans allow the use of low tin solder. High speed manufacturing of cans requires an alloy having a very narrow freezing range.

Lead–tin alloys containing 40–50 wt% tin are used for general-purpose soldering. Low melting lead–tin solder having 63 wt% tin is used for electronic soldering, particularly for printed circuit boards. Lead alloys having 15–30 wt% tin are used for soldering automobile radiators and other types of heat exchangers. A lead alloy containing 2.5 wt% tin and 0.5 wt% silver is used when high temperature fatigue and creep strengths are required, for example, in soldered connections in heat exchangers. Solders having 35–40 wt% tin have a wide plastic range and are used for wiping lead joints. Sometimes 0.5–2.0 wt% antimony is added to improve mechanical properties. Antimony contents of 0.2–0.5 wt% prevent brittle phase transformations at low temperature. Lead–tin solder alloys are listed in ASTM B32-93 (52).

Corrosion Protection. Lead–tin alloys are used for corrosion-resistant coatings on steel and copper (see METALLIC COATINGS, SURVEY). Terne steel is steel sheet coated with a lead alloy containing 15–20 wt% tin. This alloy contains sufficient tin to alloy with the surface of the steel. Terne sheets are produced flat or coiled, carrying different coating weights. These coated sheets are used

for radio and television chassis, roofs, fuel tanks, air filters, oil filters, gaskets, metal furniture, gutters, and downspouts. Terne steel has good corrosion resistance, draws well, is relatively cheap, and offers a good base for painting.

A similar coating, containing 4 wt% tin, is applied to copper sheet and is used primarily for building flashings. Other lead–tin alloys, usually with 50 wt% tin, are applied as coatings to steel and copper electronic components for corrosion protection, appearance, and ease of soldering. Lead–tin alloys can be built up easily to any desired thickness by electroplating (qv) from a fluoborate solution. Electroplated coatings are not recommended for corrosion protection because these tend to be porous (see ELECTRONICS, COATINGS).

Tin is also used as an alloying element in lead–antimony alloys to improve fluidity and to prevent drossing, in lead–calcium alloys to improve mechanical properties and enhance electrochemical performance, in lead–arsenic alloys to maintain a stable composition, and as an additive to low melting alloys.

Lead–tin (1.8–2.5 wt%) is used both as a cable sheathing alloy (BS 801 alloy A and DIN 17640) and as a battery connector alloy in sealed lead–calcium–tin batteries (15). Tin is generally added to lead–arsenic cable alloys in small amounts. The arsenic alloys have excellent creep resistance and mechanical properties, but are unstable and lose arsenic readily by oxidation. The addition of small amounts of tin (0.10–0.20 wt%) eliminates arsenic loss. Lead alloys having 0.4 wt% tin and 0.15 % cadmium, which are used for cable sheathing, do not age harden, show excellent corrosion and creep resistance, and are very ductile.

10.7. Low Melting Alloys. Lead alloys having large amounts of bismuth, tin, cadmium, and indium that melt at relatively low (10–183°C) temperatures are known as fusible or low melting alloys. The specifications of many of these alloys are listed in ASTM B774-87 (52).

These alloys are used as fuses, sprinkler system alloys, foundry pattern alloys, molds, dies, punches, cores, and mandrels where the low melting alloy is often melted out of a mold. The alloys are also used as solders, for the replication of human body parts (see BIOMATERIALS, PROSTHETICS, AND BIOMEDICAL DEVICES), and as filler for tube bending. Lead–indium alloys are often used to join metals to glass.

10.8. Reactive Lead Alloys. Strontium–lead alloys behave similarly to lead–calcium alloys in terms of mechanical properties and performance. Lead–strontium (0.08–0.20 wt%) alloys, also containing aluminum, have been used as battery grid alloys. These have excellent fluidity, harden rapidly, and have excellent resistance to corrosion. However, these alloys over-age rapidly, resulting in significant loss of mechanical strength within several days. The addition of 1 wt% or more of tin is required to resist over-aging. The high cost of lead–strontium alloys compared to lead–calcium alloys has restricted usage. Lead–strontium–tin alloys are used as anodes for copper electrowinning.

Lead–lithium and lead–lithium–tin alloys have been used as alloys for lead–acid battery grids because of very rapid aging and very high mechanical properties. These alloys are, however, susceptible to grain boundary corrosion. Lead–lithium alloys containing strontium, barium, and calcium have been used for bearings. The high melting point and the retention of mechanical properties and stability at high temperatures make these alloys particularly

attractive for bearings. The addition of aluminum to prevent oxidation permits casting at high temperatures without oxidation.

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Table 1. **World Mine Production, Reserves, and Reserve Base,** $\times$ **10^3 t**[a]

Country	Mine production 2003	2004[b]	Reserves	Reserve base
United States	460	440	8,100	20,000
Australia	694	680	15,000	28,000
Canada	150	80	2,000	9,000
China	660	950	11,000	36,000
Kazakhstan	40	44	5,000	7,000
Mexico	140	150	1,500	2,000
Morocco	38	41	500	1,000
Peru	308	300	3,500	4,000
South Africa	40	36	400	700
Sweden	50	61	500	1,000
other countries	370	370	19,000	30,000
World total (rounded)	*2,950*	*3,150*	*67,000*	*140,000*

[a]Ref. 1.
[b]Estimated.

Table 2. **Physical Properties of Lead**

Property	Value
at. wt	207.2
melting point, °C	327.4
boiling point, °C	1770
specific gravity, °C	
20	11.35
327 (solid)	11.00
327 (liquid)	10.67
specific heat, J/(kg·K)[a]	130
latent heat of fusion, J/g[a]	25
latent heat of vaporization, J/g[a]	860
vapor pressure, kPa[b]	
at 980°C	0.133
1160°C	1.33
1420°C	13.33
1500°C	26.7
1600°C	53.3
thermal conductivity,[c] W/(nK)	
at 28°C	34.7
100°C	33.0
327°C (solid)	30.5
327°C (liquid)	24.6
coefficient of linear expansion at 20°C, °C^{-1}	29.1×10^{-6}
electrical resistivity, μΩ/cm	
at 20°C	20.65
100°C	27.02
330°C	96.73
specific conductance,[d] $(\Omega m)^{-1}$	
at 0°C	5.05×10^{4}
18°C	4.83×10^{4}
327.4°C (liquid)	1.06
normal electrode potential, vs standard hydrogen electrode = 0, V	0.22
electrochemical equivalent of Pb^{2+}, g/(Ah)	3.8651
velocity of sound in lead, cm/s	122,700
surface tension at 360°C, mN/m(=dyn/cm)	442
viscosity, mPa(=cP)	
at 440°C	2.12
550°C	1.70
845°C	1.19
magnetic susceptibility at 20°C, m^3/kg[e]	-0.29×10^{-6}
hardness	
Mohs'	1.5
Brinell	
common lead	3.2–4.5
chemical lead	4.5–6
Young's modulus, GPa[f]	16.5
tensile strength, common lead, kPa[f]	
at −100°C	42,000
20°C	14,000
150°C	5,000
elongation in 5-cm gauge length, %	50–60

[a]To convert J to cal, divide by 4.184.
[b]To convert kPa to mm Hg, multiply by 7.5.
[c]Thermal conductivity relative to Ag = 100 is 8.2.
[d]Electrical conductivity relative to Cu = 100 is 7.8.
[e]To convert m^3/kg to cmu/g, multiply by 79.3.
[f]To convert GPa to psi, multiply by 145,000.

Table 3. **Lead Concentrate Composition**

Constituent	Wt%	Constituent	Wt%
Pb	45–75	Sb	0.1–2
Zn	0–15	Fe	1.0–8.0
Au	0–0.01	insolubles	0.5–4
Ag	0–0.15	CaO	trace–3.0
Cu	0–3	S	10–30
As	0.01–0.4	Bi	trace–0.1

Table 4. **Alternative Lead Smelting Processes**

Process name	Smelting type	Special features
Continuous process		
Kivcet	reaction between gases and solids, ie, flash	integral electric furnace for slag reduction; water-cooled wall separates the smelting and reduction atmospheres
QSL	reactions between liquids, ie, bath	shielded tuyeres; vessel can be rotated to protect tuyeres; internal wall separates smelting and reduction zones
Isasmelt	bath	air-cooled lance from top; oxidation and reduction vessels connected by a launder
Batch process		
Boliden Kaldo	flash and some bath reactions	top-blown vessel using a water-cooled lance; vessel rotates during smelting and reduction, and can be tilted for tapping

Table 5. **Composition of Products from Copper Dross Treatment**

Constituent	Composition, wt%	
	Using soda process[a]	Without soda process[b]
Au	0.002	0.005
Ag	0.085	0.075
Pb	9.0	17.7
Cu	52.5	39.6
As	6.6	8.4
Sb	1.2	1.9
Ni	0.1	0.1

[a]The Cu:Pb ratio is 5.8:1.
[b]The Cu:Pb ratio is 2.2:1.

Table 6. **U.S. Economic Statistics**[a]

Salient statistics	2000	2001	2002	2003	2004[b]
production					
mine, lead in concentrates	465	466	451	460	440
primary refinery	341	290	262	245	W
secondary refinery, old scrap	1,080	1,040	1,070	1,110	1,170
imports for consumption, lead in concentrates	31	2	[c]		
exports, lead in concentrates	117	181	241	253	275
imports for consumption, refined metal, wrought and unwrought	366	284	218	183	190
export, refined metal, wrought and unwrought	49	35	43	123	92
shipments from Government stockpile excesses, metal	32	41	6	60	44
consumption:					
reported	1,720	1,550	1,440	1,390	1,420
apparent	1,780	1,640	1,450	1,440	1,520
price, average, cents per pound					
North American Producer	43.6	43.6	43.6	43.8	53
London Metal Exchange	20.6	21.6	20.5	23.3	39
stocks, metal, producers, consumers, yearend	124	100	111	107	60
employment:					
mine and mill (peak), number	1,100	1,100	930	830	880
primary smeller, refineries	450	400	320	320	240
secondary smelter, refineries	1,700	1,600	1,600	1,600	1,600
net import reliance as a percentage of apparent consumption	13	8	e[d]	E[d]	E[d]

[a]Ref. 1.
[b]Estimated.
[c]Less than 1/2 unit.
[d]E = net exporter.

Table 7. **Standard Specifications for Refined Lead**[a,b]

Metal, wt%	Grade			
	Low bismuth, low silver, pure lead[c]	Refined pure lead[d]	Pure lead	Chemical copper−lead[e]
Sb	0.0005	0.0005	0.001	0.001
As	0.0005	0.0005	0.001	0.001
Sn	0.0005	0.0005	0.001	0.001
Sb, As, and Sn			0.002	0.002
Cu	0.0010	0.0010	0.0015	0.040−0.080
Ag	0.0010	0.0025	0.005	0.020
Bi	0.0015	0.025	0.05	0.025
Zn	0.0005	0.0005	0.001	0.001
Te	0.0001	0.0001		
Ni	0.0002	0.0002	0.001	0.002
Fe	0.0002	0.001	0.001	0.002
lead[f]	99.995	99.97	99.94	99.90
UNS number	L50006	L50021	L50049	L51121

[a]ASTM B29-92. Values given are maximum allowable unless range is given.

[b]By agreement between the purchaser and the supplier, analyses may also be required and limits established for elements or compounds not specified.

[c]This grade is intended for chemical applications requiring low silver and bismuth contents.

[d]This grade is intended for lead−acid battery applications.

[e]This grade is intended for applications requiring corrosion protection and formability.

[f]Value for lead is minimum value, determined by difference.

Table 8. **U.S. Consumption of Lead by Product, t**[a]

SIC code	Product	2001	2002
	metal products		
3482	ammunition, shot and bullets	53,600	57,600
	bearing metals		
35	machinery except electrical	W	W
36	electrical and electronic equipment	W	W
371	motor vehicles and equipment	498	374
37	other transportation equipment	W	W
	Total	*837*	*406*
3351	brass and bronze, billets and ingots	2,590	2,730
36	cable covering, power and communication	W	W
15	calking lead, building construction	927	1,060
	casting metals		
36	electrical machinery and equipment	W	W
371	motor vehicles and equipment	24,100	29,400
37	other transportation equipment	W	W
3443	nuclear radiation shielding	2,360	1,290
	Total	*31,800*	*34,800*
	pipes, traps, other extruded products		
15	building construction	2,370	2,250
3443	storage tanks, process vessels, etc.	[b]	[b]
	Total	*2,370*	*2,250*
	sheet lead:		
15	building construction	16,300	18,100
3443	storage tanks, process vessels, etc.	[b]	[b]
3693	medical radiation shielding	6,080	7,550
	Total	*22,400*	*25,600*
	solder:		
15	building construction	1,190	1,320
	metal cans and shipping containers	W	W
367	electronic components, accessories and other electrical equipment	3,690	3,970
371	motor vehicles and equipment	W	W
	Total	*6,120*	*6,450*
	storage batteries		
3691	storage battery grids, post, etc.	655,000	554,000
3691	storage battery oxides	694,000	641,000
	Total storage batteries	*1,350,000*	*1,190,000*
371	terne metal, motor vehicles and equipment	[c]	[c]
27	type metal, printing and allied industries	[d]	[d]
34	other metal products[e]	17,100	24,200
	Total	*1,490,000*	*1,350,000*
	other oxides		
285	paint	W	W
32	glass and ceramics products	W	W
28	other pigments and chemicals	W	W
	Total	*43,900*	*51,900*
	miscellaneous uses	14,500	34,200
	Grand total	*1,550,000*	*1,440,000*

[a]Ref. 45, W Withheld to avoid disclosing company proprietary data; included appropriate totals.
[b]Included with "Building construction" to avoid disclosing company proprietary data.
[c]Included with "Bearing metals, motor vehicles and equipments."
[d]Included with "Other metal products" to avoid disclosing company proprietary data.
[e]Includes lead consumed in foil, collapsible tubes, annealing, galvanizing plating, electrowinning, and fishing weights.

Table 9. **Mechanical Properties of Lead–Antimony Alloys**[a]

Antimony content, wt%	Yield strength after aging, MPa[b,c]		Tensile strength, MPa[b]	Elongation, %
11	68.9	74.4	75.9	5
6	55.2	71.0	73.8	8
3	34.0	55.2	65.5	10
2	24.1	37.9	46.9	15
1	13.8	19.3	37.9	20
0	3.5	3.5	11.7	55

[a]After 30 days, unless otherwise noted.
[b]To convert MPa to psi, multiply by 145.
[c]Column on left is after one day.

Table 10. **Printing Alloys**

Process	Composition, wt%			Temperature		Brinell hardness
	Sn	Sb	Pb	Liquidus, C°	Solidus, C°	
linotype	4	11.5	84.5	243	239	22
electrotype	3	3	94	299	245	14
stereotype	5	14	81	256	240	23
monotype	7	16.5	76.5	275	240	26
foundry type	14	24	62	318	240	32

Table 11. **Mechanical Properties of Pure Lead and Lead Alloys**

Property	Pure lead	Lead alloys		
		0.06 wt % Cu	1 wt % Sb	0.04 wt % Ca
tensile strength, MPa	12.2	17.4	20.9	27.9
elongation, %	55	55	35	35
fatigue strength, MPa[a]	2.75	4.90	6.28	9.02

[a]To convert MPa to psi, multiply by 145.

Table 12. **Mechanical Properties of Cast Lead Alloys**

Property	Lead alloy components, wt %						
	Cu 0.06	Ca 0.06	Ca 0.04, Sn 0.50	Ca 0.08, Sn 0.30	Ca 0.08, Sn 0.50	Ca 0.08, Sn 1.0	Sb 6.0
tensile strength, MPa[a]	17.4	34.8	41.8	46.0	48.8	59.7	59.2
yield strength, MPa[a]	9.0	24.3	27.9	34.8	38.2	46.0	55.8
elongation, %	55	30	15	20	15	15	15
time to failure,[b] h		10	30	50	100	450	>10,000

[a]To convert MPa to psi, multiply by 145.
[b]At 20.9 MPa.

Table 13. **Mechanical Properties of Rolled Lead Alloys]**

Property	Lead alloy components, wt %					
	Cu 0.06	Ca 0.06	Ca 0.04, Sn 0.50	Ca 0.065, Sn 0.70	Ca 0.06, Sn 1.30	Sb 6.0
tensile strength, MPa[a]	17.4	32.8	48.8	62.8	69.6	30.6
yield strength, MPa	9.0	25.1	46.0	59.2	66.2	19.5
elongation, %	55	35	15	10	10	35
time to failure[b], h		7	850	3,000	>10,000	1.5

[a]To convert MPa to psi, multiply by 145.
[b]At 20.9 MPa.
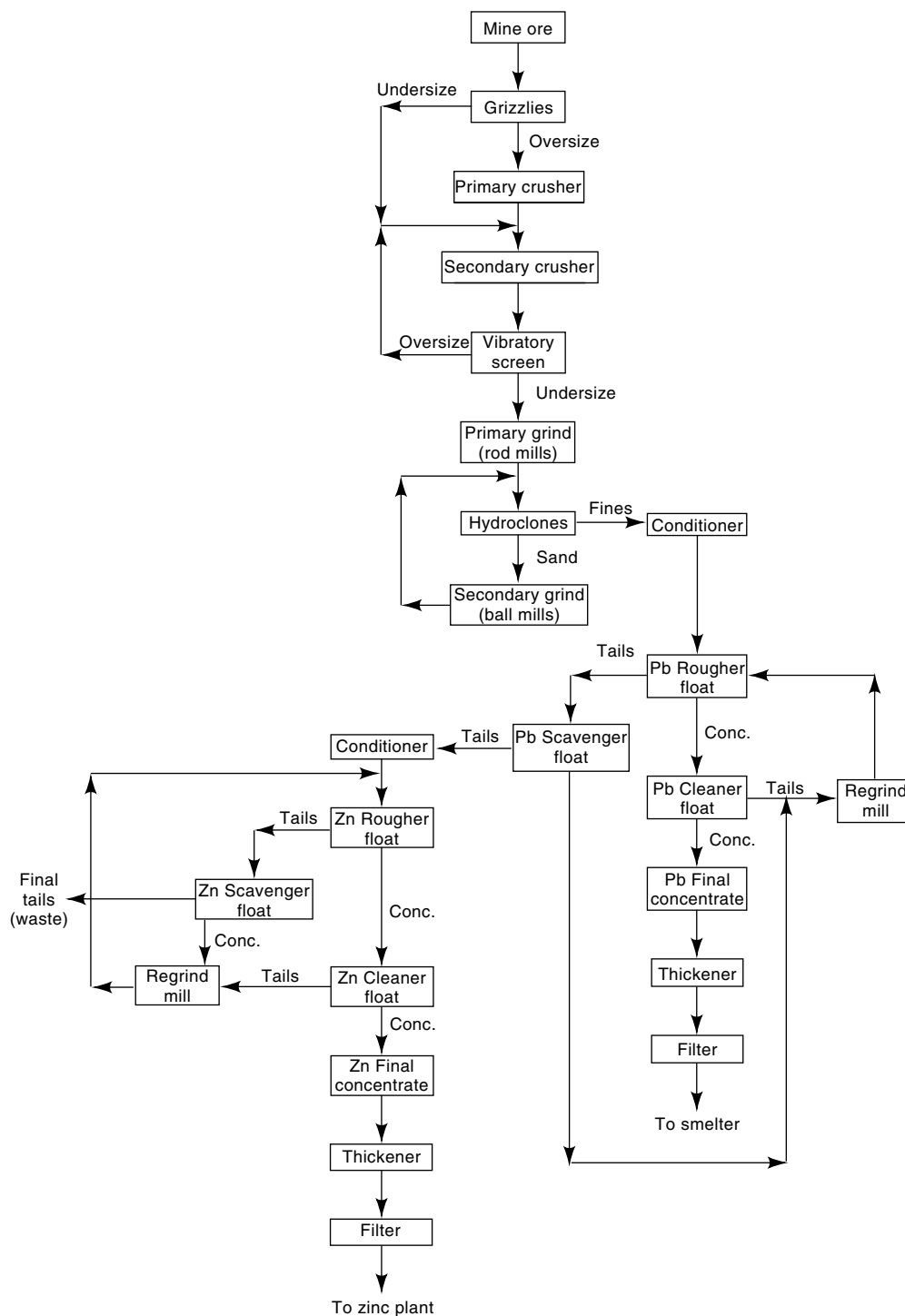
Fig. 1.   Beneficiation of mixed lead–zinc ores.

Gas outlet

Hood

Sinter cake

Lubricated seal
bar

Sand seal

Pallet

Working floor

Dust trapper

Windbox

Air
inlet

Dust hopper

Pallet return

Return rail

Windbox clearing
chute
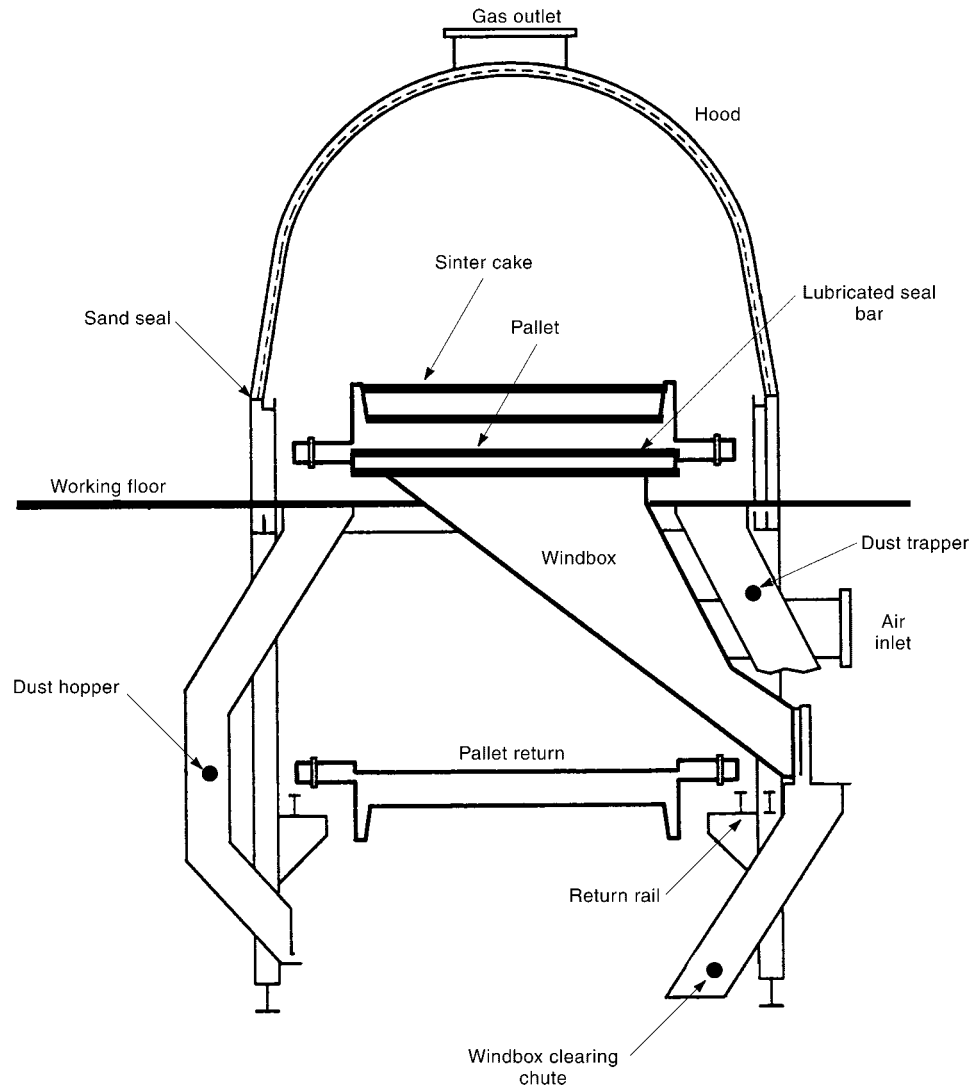
Fig. 2.   Cross section of a lead sinter machine.
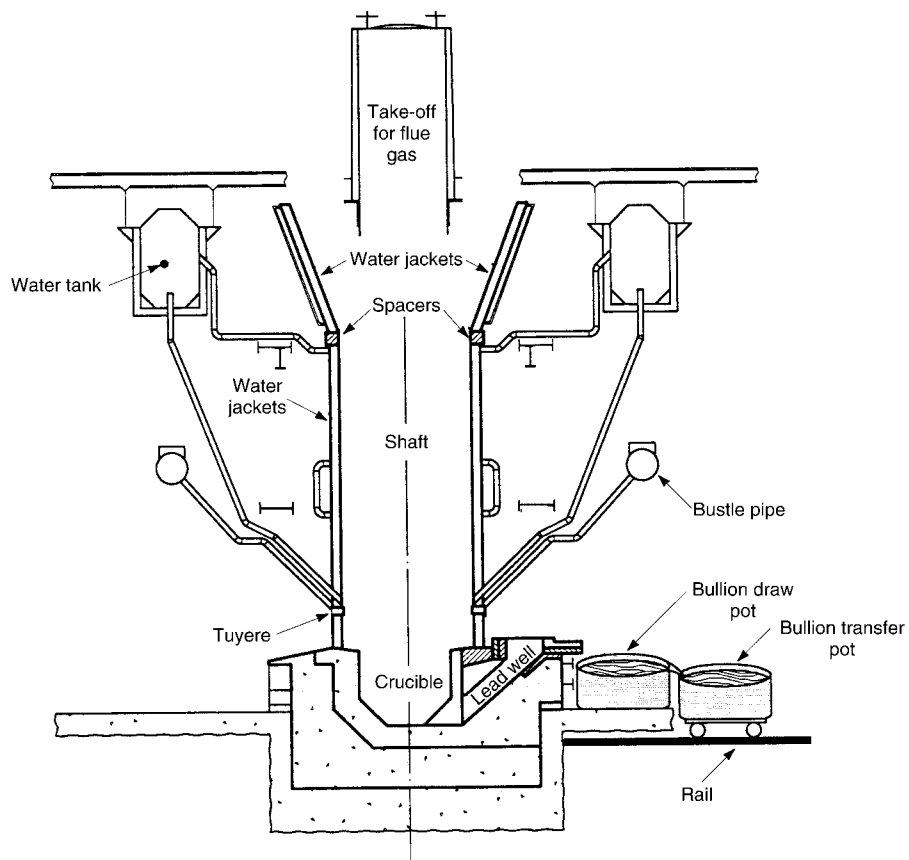
Fig. 3. Cross section of lead blast furnace.
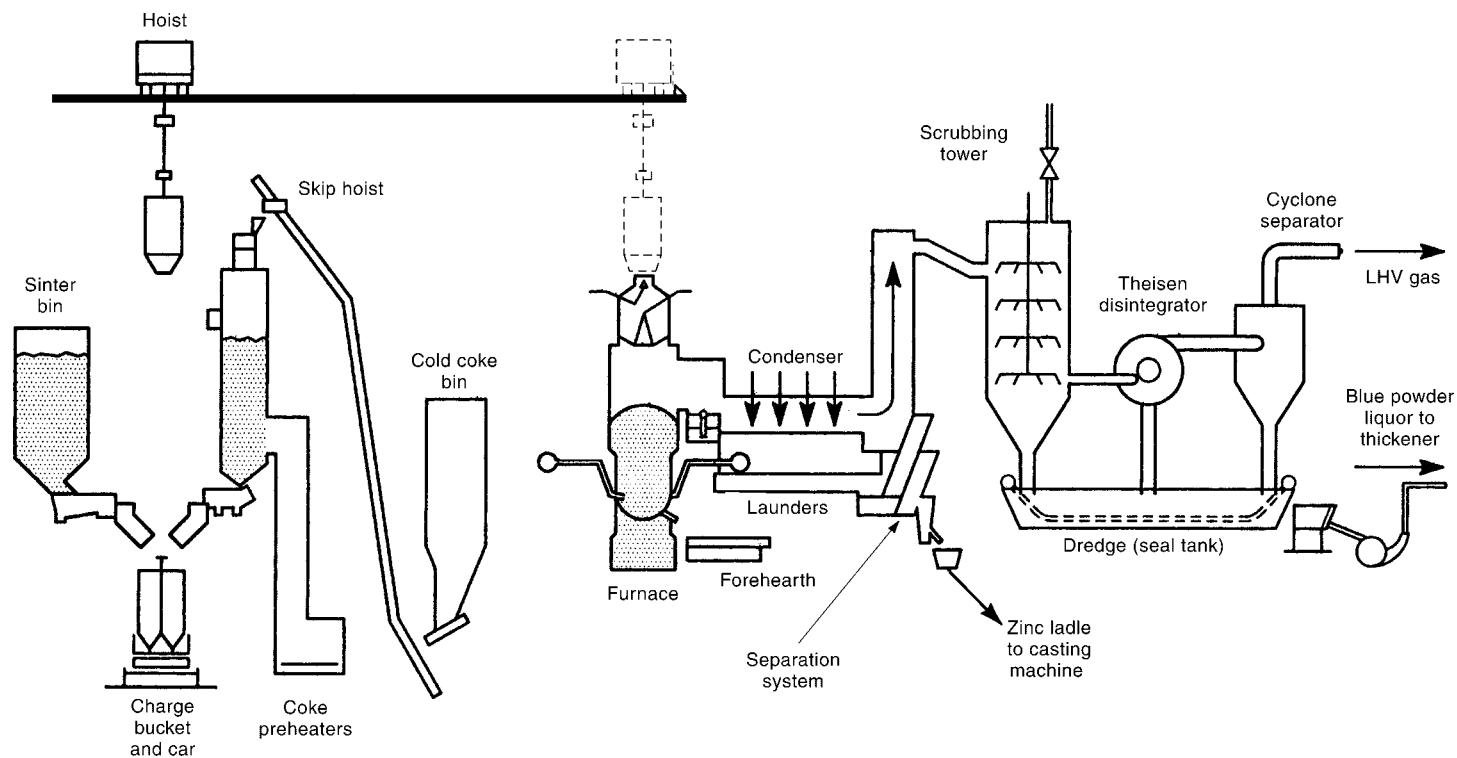
Fig. 4. Schematic illustration of an Imperial smelting furnace plant. LHV = low heating value.
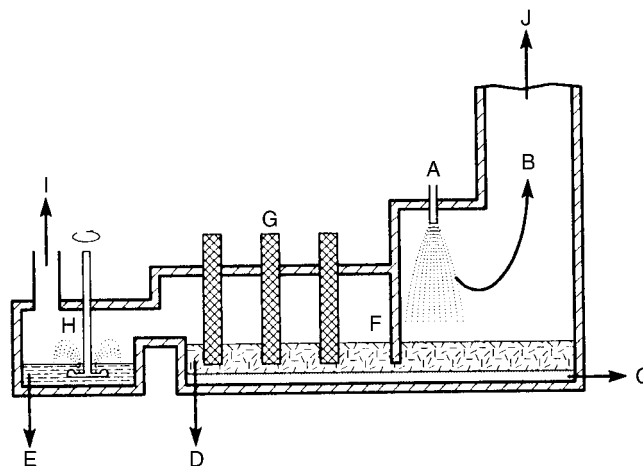
Fig. 5.   Kivcet process: A, concentrate burner; B, fume-laden gas; C, lead tap; D, slag tap; E, zinc tap; F, water-cooled underflow wall; G, electrodes; H, lead-splash condenser; I, CO off-gas; and J, to electrostatic precipitator.
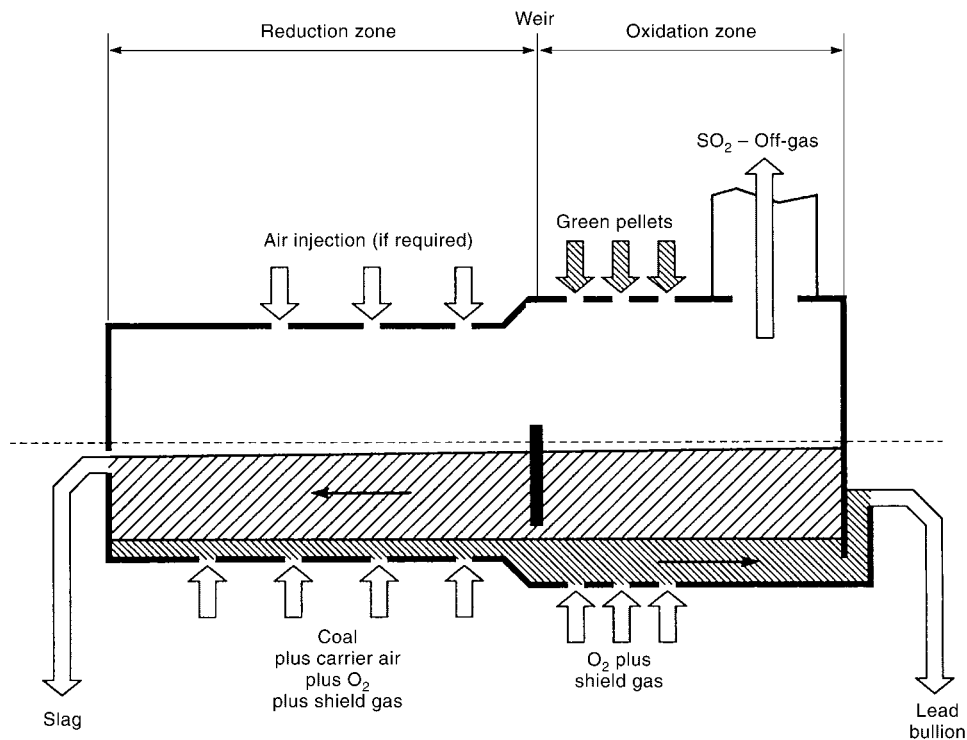
Fig. 6.   QSL furnace. The green pellets consist of concentrate, fluxes, flue dust, and coal.
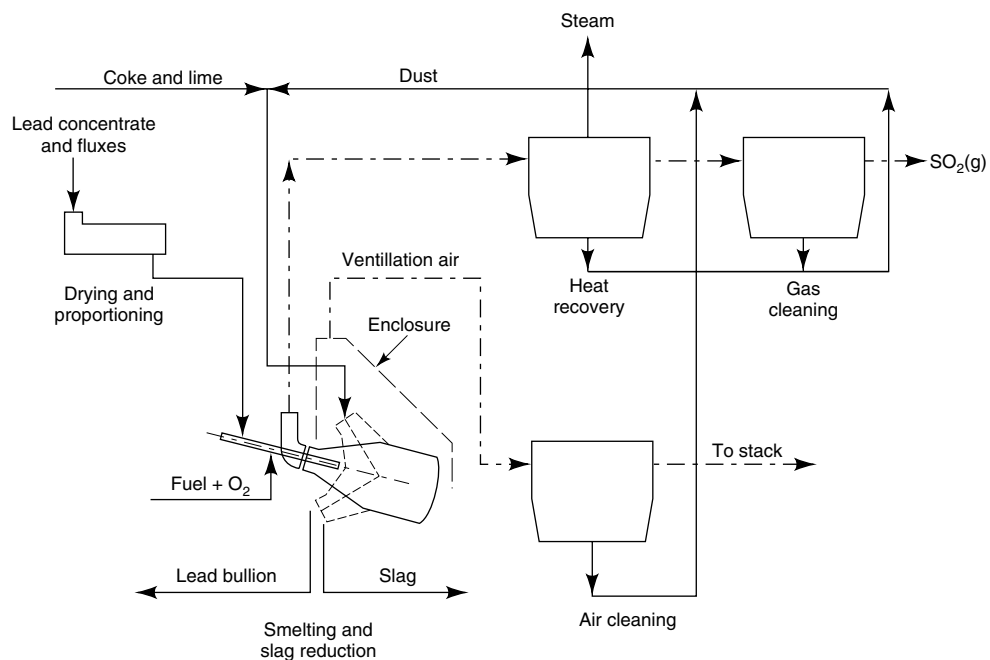
Fig. 7.   Boliden Kaldo lead smelting process.
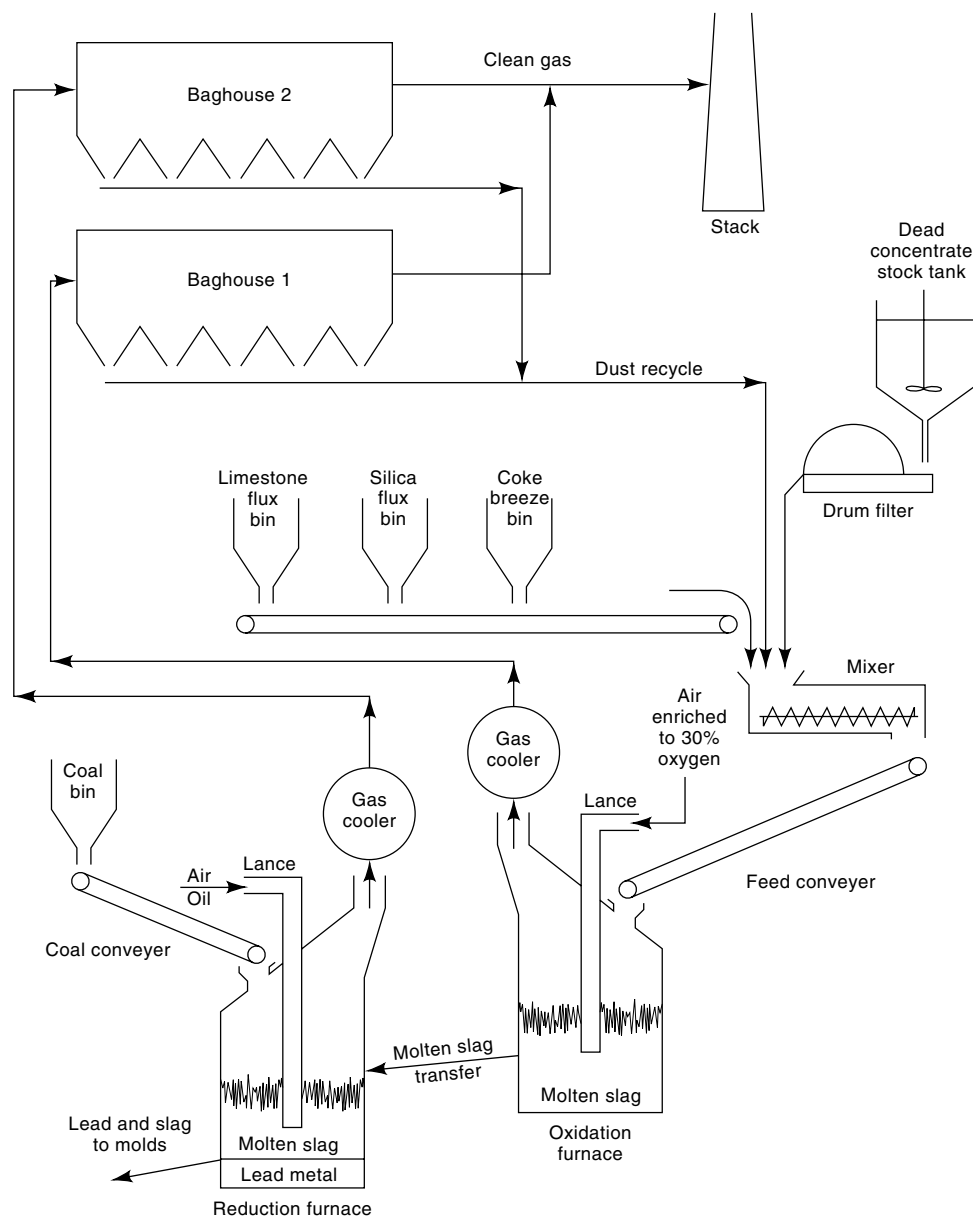
Fig. 8. Schematic diagram of the Isasmelt process.
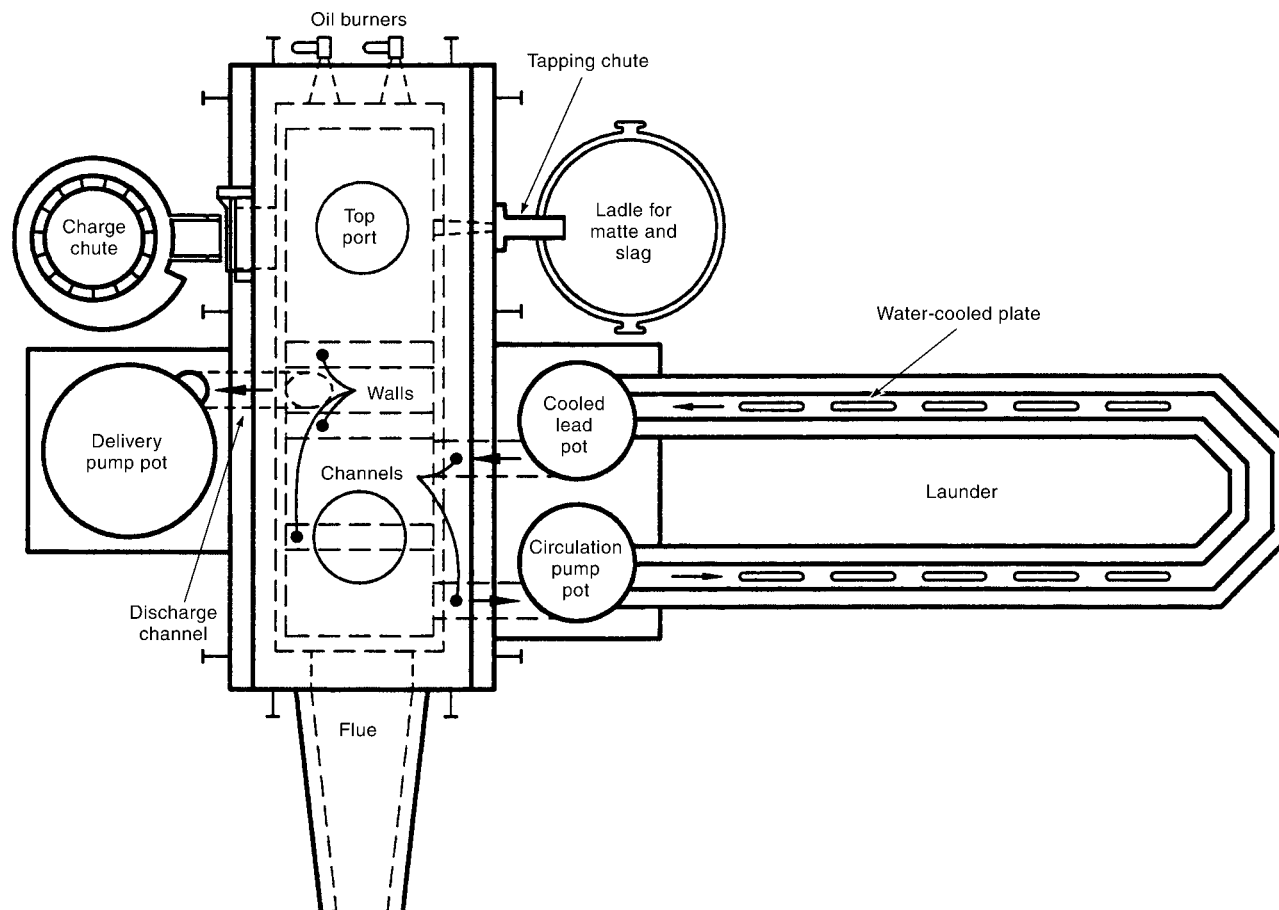
Fig. 9. Continuous drossing of lead bullion.
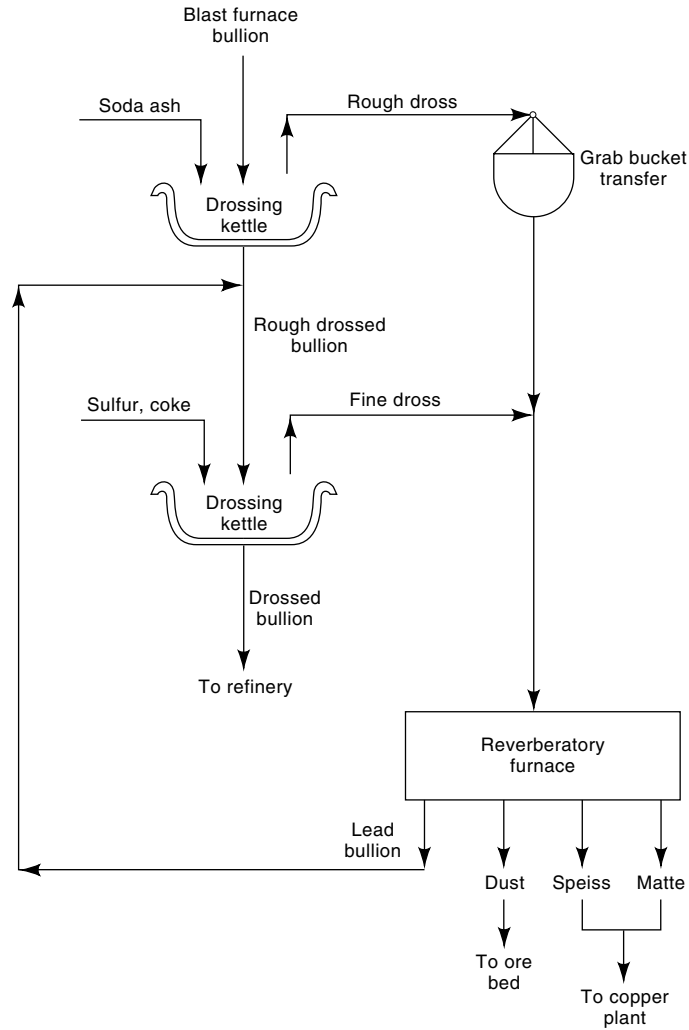
Fig. 10.   Soda drossing process.
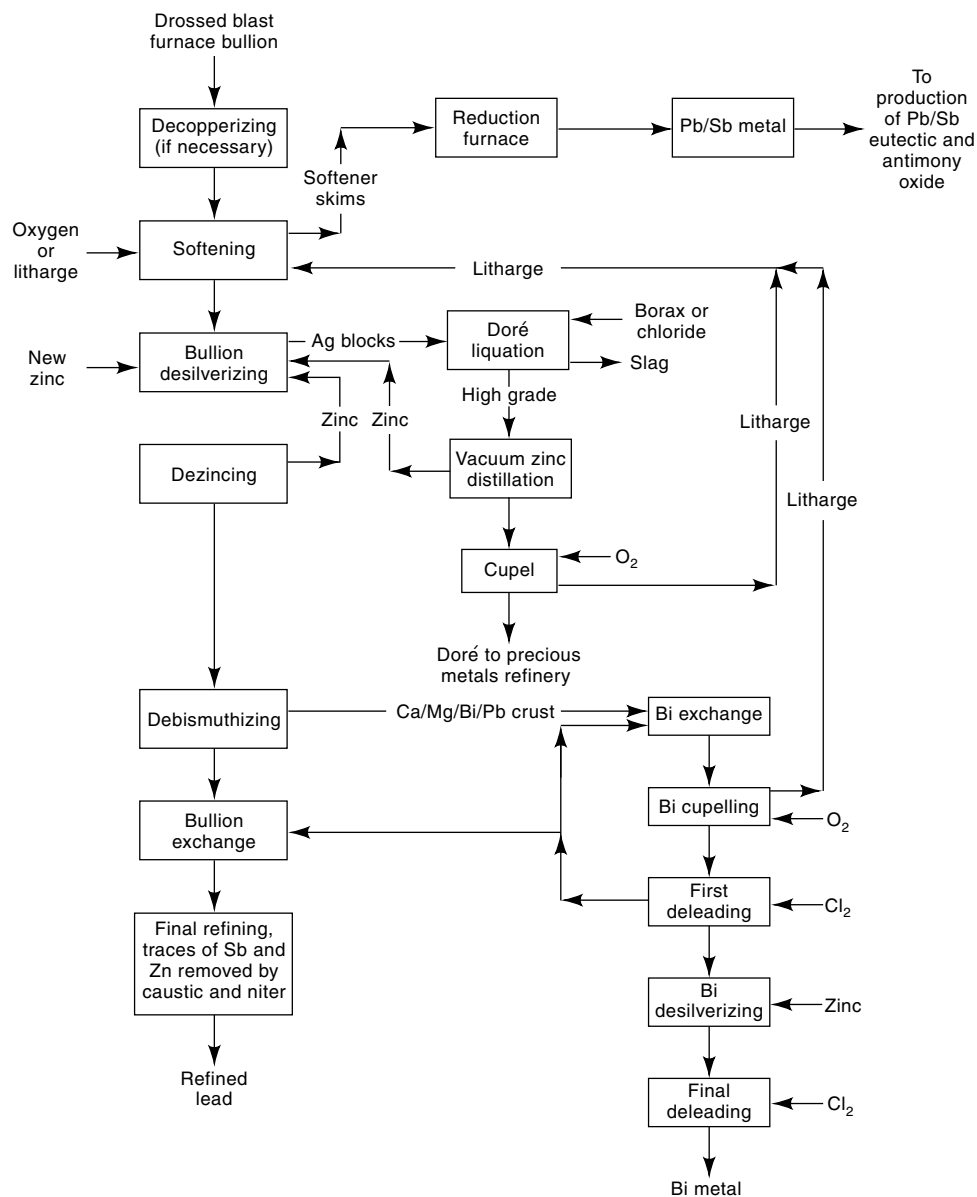
Fig. 11. Flow diagram of a furnace-kettle and/or all-kettle lead refining process.
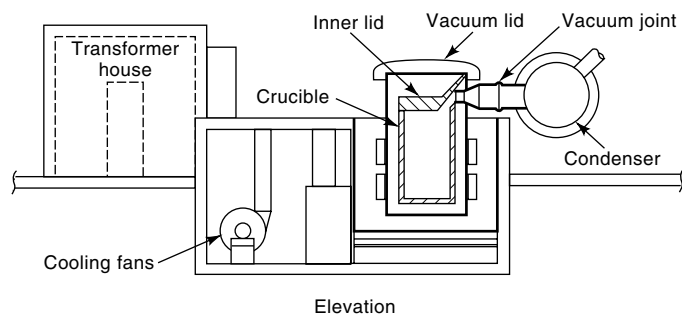
Fig. 12.   Hoboken vacuum retort.
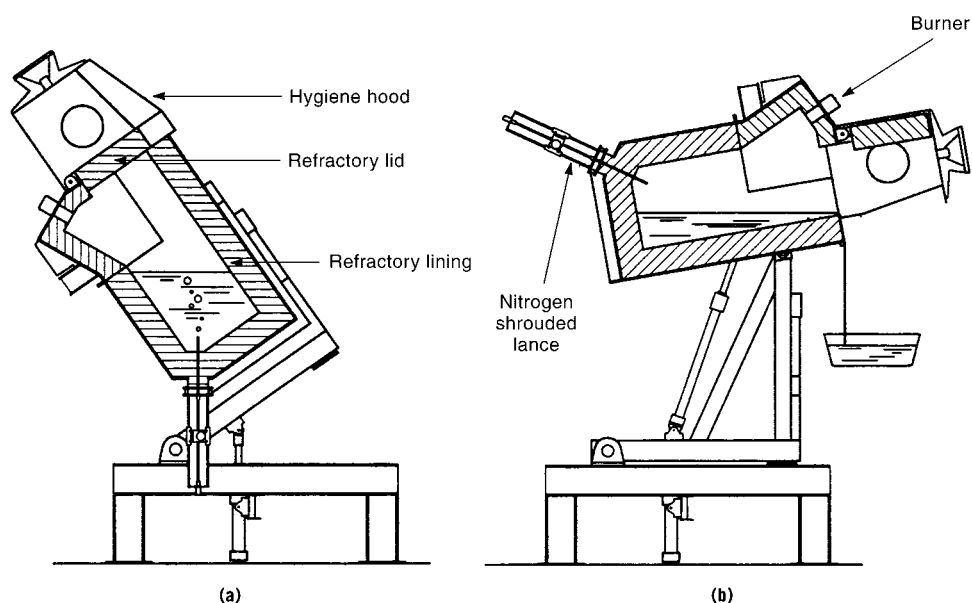
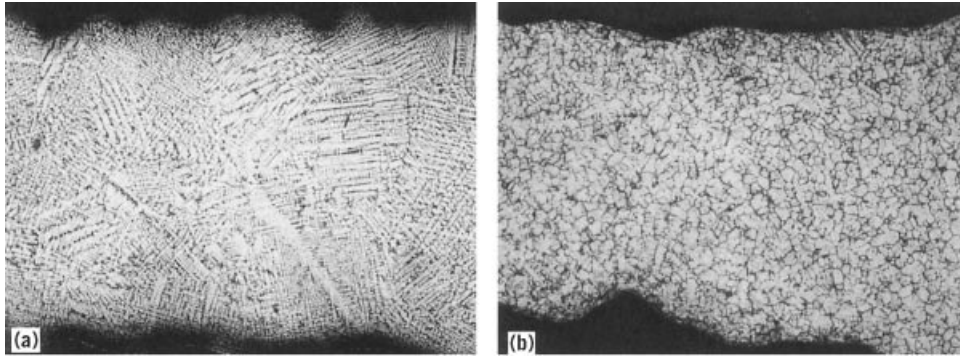**Fig. 13.**   Bottom blown oxygen cupel (BBOC) in positions for (**a**) blowing oxygen and (**b**) tapping slag.
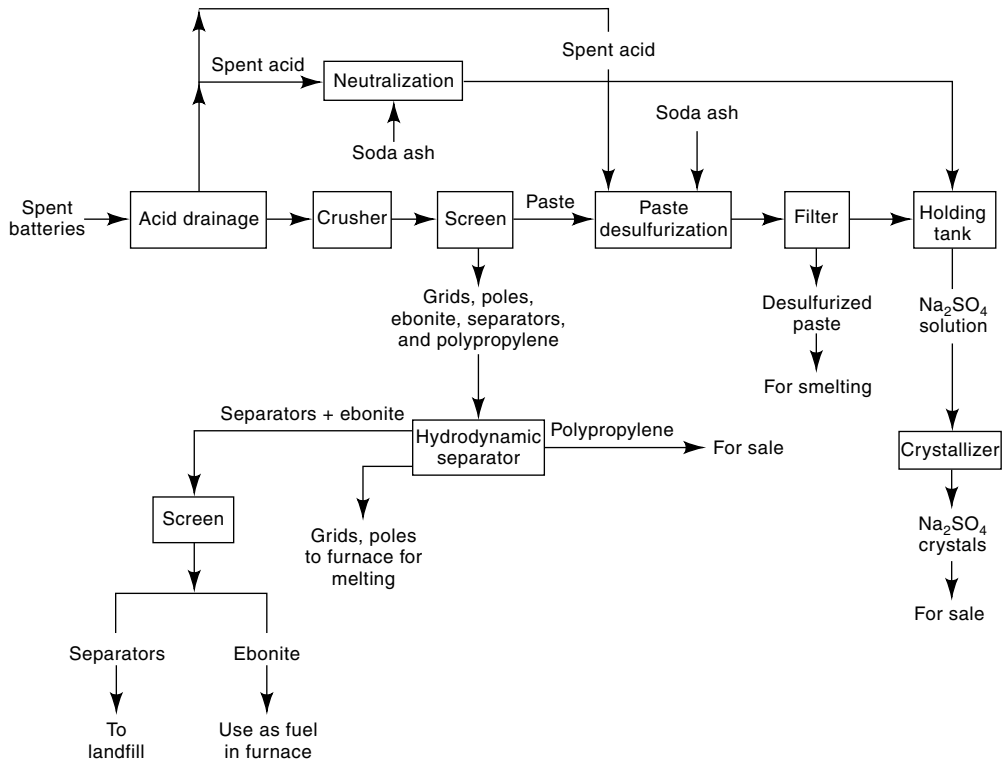
**Fig. 14.** Schematic flow sheet for a typical spent battery breaking operation.
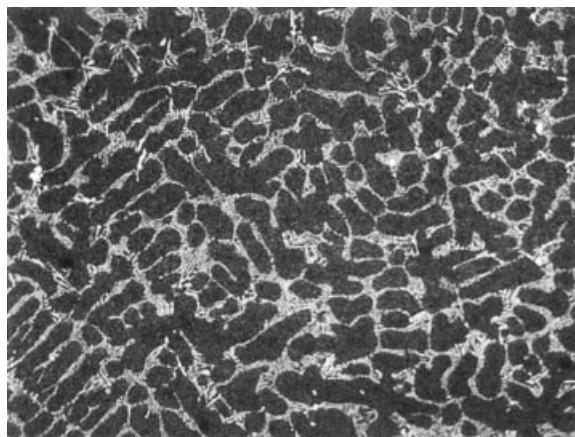
Fig. 15. Grain structure of cast lead−6 wt% antimony alloy showing the dark lead, white antimony eutectic particles at a magnification of 160×.

Fig. 16.   Grain structure of lead−2 wt% antimony alloy battery grid at a magnification of 50×: (**a**) no nucleants; (**b**) containing 0.025 wt% selenium as a grain refiner.
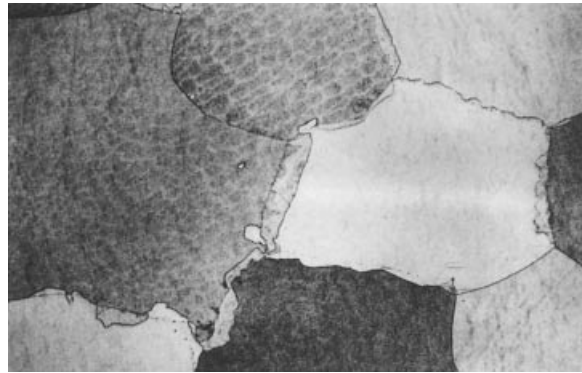
Fig. 17.   Large columnar as-cast grain structure of lead−calcium alloys at a magnification of 80×.
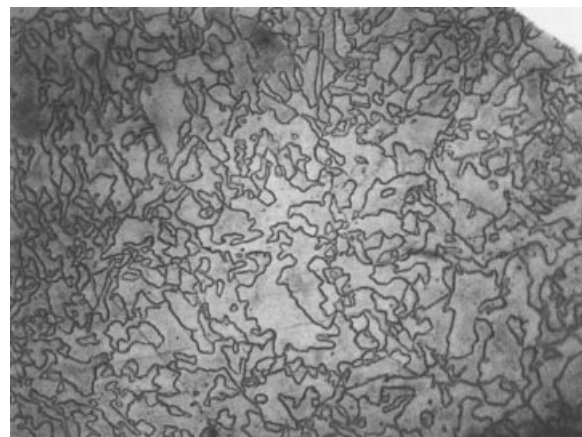
Fig. 18.   Grain structure of lead−0.07 wt% calcium alloy aged for seven days showing serrated grain boundaries at a magnification of 320×.