### CHAPTER 12.19

# Lead and Bismuth

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## LEAD

Lead is a soft, ductile, bluish-white, dense metallic element and ranks fourth in world nonferrous metal consumption after aluminum, copper, and zinc. Lead possesses several unique properties that distinguish it from other common metals, and its ease of fabrication makes it useful in a wide range of applications. It has a comparatively high-density, low melting point; low electrical conductivity; and little mechanical strength. In addition, pure lead is soft and malleable and has outstanding corrosion resistance. The first use of lead dates far back in history to 4000 BC when a figurine was found in Egypt and is recognized as the oldest lead article. Later, because of its malleability and corrosion resistance, lead was used expansively by the Romans for water pipes, aqueducts, tank linings, and cooking pots, and then by scientists in early cosmetics, paints and pigments, and lead-rich glazes (ILA 2018). From its origins and early development in Europe, and later in North America, the lead industry has expanded enormously in the modern era. Lead also readily forms alloys and compounds and is used in many commercially important alloys. In this century, lead remains a foundation of society, but in a very different way. Although it is still used for its malleability and corrosion resistance, its chemical properties now make it a thoroughly modern metal (ILA 2018).

Notwithstanding this significantly changing pattern in the market segments, the volume of world production and consumption of refined lead has steadily grown more than tenfold in most countries over the last 100 years and particularly in the last ~45 years, according to published statistics by the International Lead and Zinc Study Group (Figure 1). In 2017, the production and consumption was 11.451 Mt (million metric tons) and refined lead was 11.594 Mt, respectively, despite the intense pressure from environmental and health legislation that has resulted in increasingly restrictive disposal and emission regulations. As one direct consequence, the usage of many lead-based products has been greatly diminished and some have been completely eliminated during the past three decades. These products include pigments based on lead (litharge and red lead, both oxides of lead, as well as white lead, a carbonate, were the most important ones), organo-lead-based antiknock compounds (tetraethyl lead) as a gasoline additive for automobiles, lead glazes for pottery, solder for various applications such as sealing the seams of steel cans, automobile body solder, soldering pipe connections for potable water systems, sealing copper radiators, lead pipes, lead-based metal bearings, lead sealants such as for drain pipes or for wine bottles, chemical tank linings, ammunition, and power and electrical cable sheathing. In most cases, the application was eliminated, or the products were substituted because of environmental pressures associated with the dispersive and toxic nature of lead in order to minimize the potential exposure of lead. The antiknock additives in gasoline were banned because lead terminated the functionality of the catalytic connectors on automobiles, which were employed to improve air quality. Most lead-bearing solder materials for steel cans and potable water systems were substituted because of a potential leaching of lead from these products.

Alloying lead with copper, steel, and aluminum improves its machinability and the alloys are used in bearing metals and castings even though all these applications are declining. Mainly to reduce vehicle weight, copper radiators have been replaced by aluminum. Roller bearings made of steel have replaced lead bearings, plastic pipes have replaced tile drain lines, and lead tank linings have been replaced by stainless steels. Although the consumption has gradually declined in recent years, owing to the development of competitive plastic and aluminum sheathing materials, lead cable-sheathing alloys are still used to protect power and communication cables mainly for underwater applications. Lead alloys are used in the manufacture of shot and other ammunition; however, steel shot is now used, and leaded steels are more and more being replaced with bismuth-containing alloys.

The successful substitution of lead-based products is mainly driven by use of materials with lower toxic properties and advanced mechanical properties such as less weight or increased strength. In addition, these substitutions restrict the release of lead to the environment. However, lead-based products will continue to exist because they are cost-effective, readily recyclable, not readily substituted, and packaged to limit exposure of lead. In addition, such products result in a

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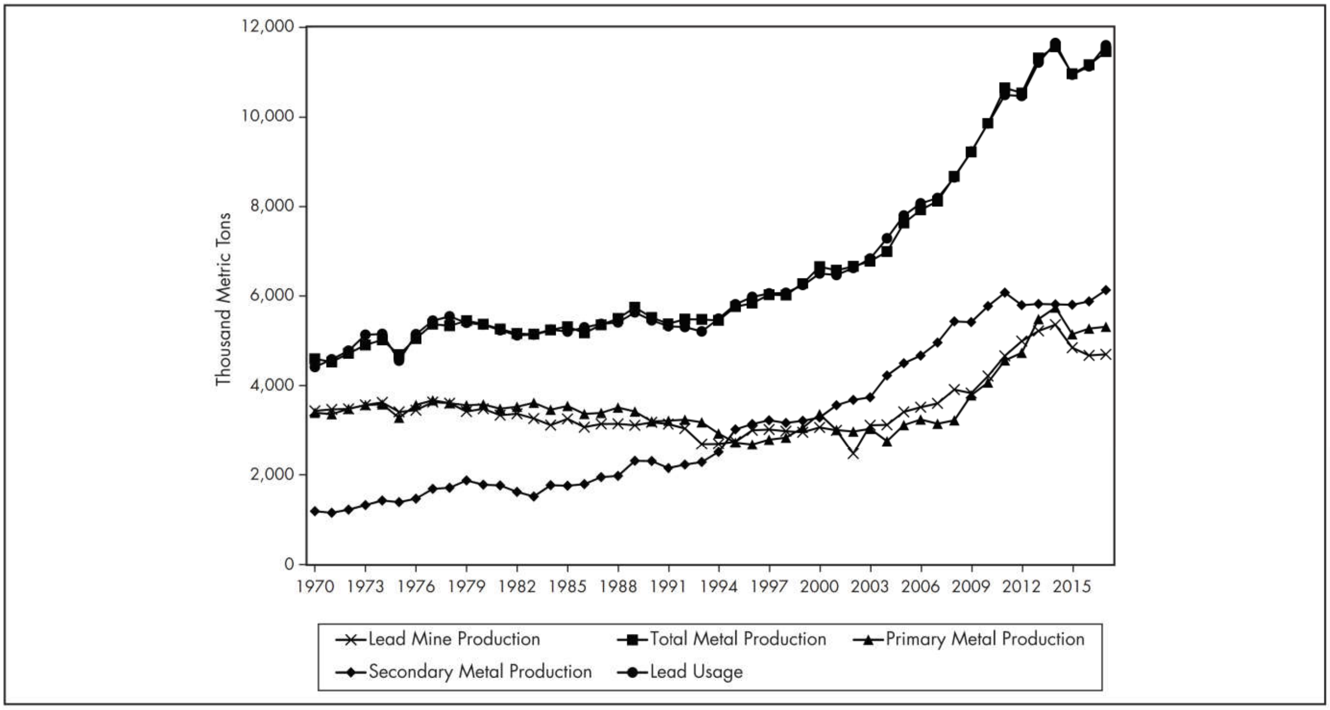


**Figure 1 World lead production and consumption from 1970–2017**

longer service life, use lower amounts of lead, or offer significant advantages over competitive materials.

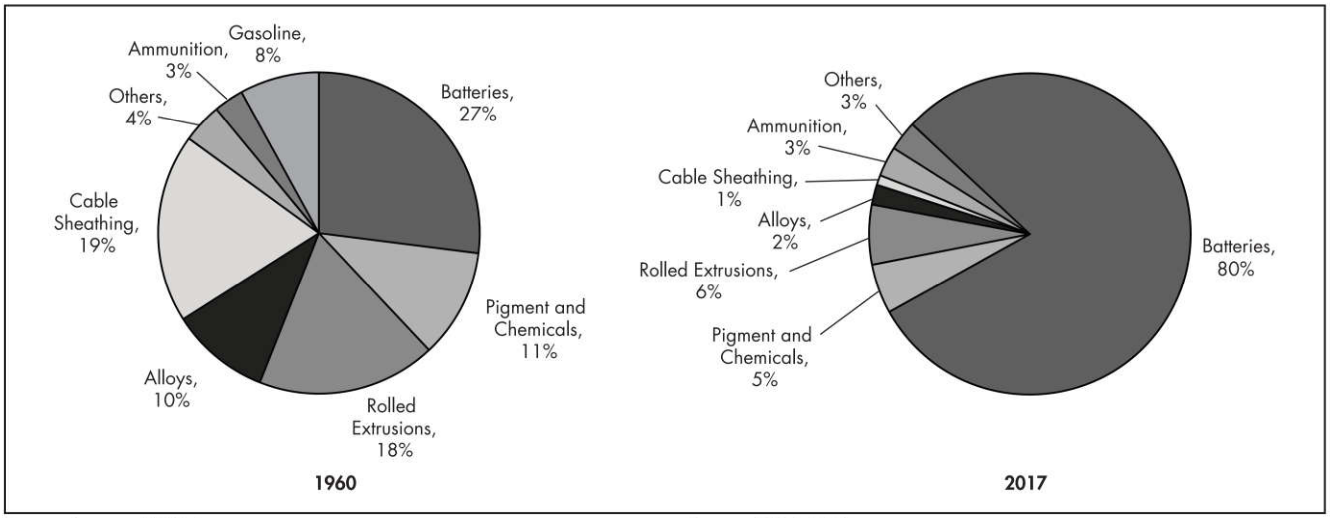
Modern lead products have special, unique properties that enable them to compete with other materials. These special characteristics are predominantly protective and electrochemical. One of the unique properties of lead is the ability to collimate and absorb X-rays and other damaging radiation. Therefore, it will continue to find significant use in protecting the population from radiation. Applications are and will continue to exist in containers for radioactive isotopes and shielding in nuclear-powered and medical treatment facilities. Lead oxide glasses will be employed in cathode ray tubes, TV picture tubes, computer screens, and transparent shielding to protect users of these products from ionizing radiation. The degradation process of polyvinylchloride (PVC) products due to ultraviolet radiation or the exposure to other natural environmental processes will be virtually prevented by means of lead stabilizers. Lead sheet will continue to be used as waterproofing where long lifetimes are required. Therefore, semi-manufactured forms of lead products for radiation shielding, sheet for roofing, collapsible tubes, compounds in the glass and plastics industries, and insoluble anodes for metal electrowinning have survived and grown. Lead is also used as an annealing medium for certain steel alloys, a constituent of zinc galvanizing baths, and as weights and ballast. Among the newer uses that have growth potential are sound insulation, dispersion-strengthened lead, and earthquake-resistant shock absorbers in the construction industry (Prengaman 2000).

Lead is able to exist in three different states (metal, ion with a +2 charge, and ion with a +4 charge). Because of this unique property, it is used not only as electrochemical anodes to electroplate other metals from sulfuric acid solution but also can serve as an anode, cathode, or active material in lead–acid storage batteries.

The principal market for lead, however, with the most dominating and fastest growing share, is for lead–acid storage batteries for the expanding population of motorized vehicles. The battery market is characterized by relatively short product life and high recycling rates. Lead–acid storage batteries are used as starter batteries in vehicles, which supplies starting, lighting, and ignition, but also as industrial batteries in emergency systems, computer installations, fork-lift trucks, golf carts, other non-highway vehicles, and marine equipment. Moreover, they are used to a growing extent for telecommunication systems, as sealed power packages for potable electrical appliances, and for uninterruptive power sources, remote access power systems, and hybrid and electric vehicles (Siegmund 2001). The change in average end-use pattern for lead over the last five and one-half decades is illustrated in Figure 2.

More than 90% of all products using lead metals are recyclable, making lead one of the most recycled materials used today. In addition, there are a significant amount of lead-containing secondary materials available from industrial processes and environmental cleanups representing a potential raw material source. One direct consequence is the continuously rising recycling rate of lead-bearing scrap. In 2017, refined lead recovered from secondary materials totaled 6.034 Mt (Figure 1), equivalent to 50.3%—more than half of total production worldwide. In the Western World, as much as 70.6% comes from secondary production. The majority of this secondary lead is produced from spent lead–acid batteries, with most of the remainder coming from other sources such as lead pipe and sheet.

Secondary lead smelting involves the recovery of metallic lead from lead-bearing scrap material generated by industrial and consumer sources. While some secondary smelters are associated with battery manufacturers, as part of an integrated



Source: Siegmund 2010

Source: ILZSG 2017

**Figure 2 Lead consumption in 1960 and 2017**

and closed production circuit, others are independently operated. These stand-alone smelters are purchasing scrap and selling metal or converting metal for customers on a toll basis. More and more primary smelters also tend to treat secondary materials. In conjunction with environmental concerns, the decreasing net lead mine output during the last two decades of the last century (which resulted in difficulties in sourcing adequate supplies of concentrates and led to temporarily high treatment charges) has resulted in intensive research into utilization of secondary materials.

## Mineralogy and Reserves

### *Occurrence*

Lead is among the less common metals in the earth's crust and much scarcer than other nonferrous metals. It has an average crustal abundance of between 10 and 15 ppm, which may rise up to 20 ppm in granites and shales. Lead is found in more than 200 different minerals but is an extremely chalcophile element like copper and zinc. Therefore, the majority of lead ores occurs in unoxidized primary sulfides and is of hydrothermal origin. In this process, metals are often leached simultaneously, giving rise to deposits containing combinations of metals. Two types of ore deposit—the stratabound, nonvolcanic deposits and the volcanic magmatic sedimentary of exhalative origin—form the basis of about 80% of current world lead reserves. Important examples of the nonvolcanic stratabound deposit are the Australian Cannington supergiant mine or deposits found in Missouri, United States (Doe Run Company). The major stratiform sedimentary deposits include Mount Isa, Century, and Broken Hill, all in Australia; the Russian Gores mine; and the Sullivan mine in Canada. The remaining 20% consists of multi-metal ore bodies such as Red Dog in Alaska, United States, which consists of a metamorphosed combination featuring both the stratabound and the stratiform ore bodies, or some structurally different stratabound deposits found in Cartagena, Spain, and Cerro de Pasco, Peru. Furthermore, some lead is mined from contact pyrometasomatic deposits. Examples are various mines in Mexico with Peñasquito as the largest, and some deposits in Sweden belonging to Boliden.

The most common and most important primary lead mineral is galena [$PbS$] with a theoretical lead content of 86.6 wt %. Other more common lead minerals are cerussite [$PbCO_3$] with 77.5% Pb, and anglesite [$PbSO_4$] with 68.3% Pb. In a few deposits, jamesonite [$Pb_4(FeSb)_7S_{14}$] with about 40% Pb and boulangerite [$Pb_5Sb_4S_{11}$] with about 58% Pb are important constituents of the ore, generally in addition to galena. Other lead minerals consist of, but are not limited to, pyromorphite [$Pb_5(PO_4)_3Cl$] with 76% Pb, vanadinite [$Pb_5(VO_4)_3Cl$], wulfenite [$Pb(MoO_4)$] with 56% Pb, and krokoite [$Pb(CrO_4)$].

Lead ores are commonly accompanied by zinc ores, with sphalerite [$ZnS$] predominating, but they are all gradations in relative proportions. Commonly associated sulfides in lead–zinc deposits are pyrite [$FeS_2$], marcasite [$FeS_2$], and chalcopyrite [$CuFeS_2$]. Less common are arsenopyrite [$FeAsS$], tetrahedrite [$(Cu,Fe,Ag)_{12}Sb_4S_{13}$], tennantite [$(Cu,Fe,Ag)_{12}As_4S_{13}$], enargite [$Cu_3AsS_4$], bornite [$Cu_5FeS_4$], and pyrrhotite [$FeS$]. Stibnite [$Sb_2S_3$] is an occasional constituent. Copper is often a minor constituent in lead–zinc ores.

Silver is an almost universal constituent of galena ore and may occur as argentite [$Ag_2S$], matildite [$AgBiS_2$], or as native silver in solid solution in the galena lattice. It may also occur in other minerals such as tetrahedrite or tennantite. The silver content of lead ores varies from <100 ppm to >4%, with an average typically between 500 ppm and 5,000 ppm. Galena with higher silver content usually has elevated concentrations of antimony and bismuth. In some instances, lead ores contain antimony, bismuth, arsenic, and selenium in recoverable concentrations.

The common gangue minerals include several carbonates, such as calcite [$CaCO_3$], dolomite [$CaMg(CO_3)$], ankerite [$Ca(Fe,Mg,Mn)(CO_3)_2$], and siderite [$FeCO_3$]. Quartz and jasperoid [$SiO_2$], fluorite [$CaF_2$], and barite [$BaSO_4$] are also common. A different assemblage of gangue minerals is found in contact metamorphic and deep vein deposits that formed at somewhat higher temperatures than most lead–zinc ores. Such deposits tend to be primarily pyrite-bearing copper deposits in which chalcopyrite and bornite are the major ore minerals, accompanied by varying but commonly substantial quantities of sphalerite, subordinate galena, and commonly

**Table 1 Top world mining operations in 2014**

| Mine and Location | Reserves, Mt | Lead Grade, % | In Situ Pb, Mt | 2014 Output, kt |
|---|---|---|---|---|
| Cannington (BHP Billiton), Australia | 20.3 | 10.8 | 2.2 | 202 |
| Doe Run, United States | 34.8 | 5.5 | 1.9 | 188 |
| Mount Isa (Glencore), Australia | 108.8 | 3.0 | 3.3 | 168 |
| Gorevsk (JSC Gorevsky), Russia | 109.1 | 6.6 | 7.2 | 155 |
| Red Dog (Teck Resources), United States | 51.3 | 4.7 | 2.4 | 110 |
| Huize Qilinchang, China | 15.0 | 10.1 | 1.5 | 100 |
| Magellan (Ivernia), Australia | 14.7 | 5.6 | 0.8 | 90 |
| Peñasquito (Goldcorp), Mexico | 547.0 | 0.3 | 1.7 | 70 |
| Century (MMG), Australia | 58.3 | 1.2 | 0.7 | 64 |
| Fankou (Zhongjin Lingnan), China | 35.8 | 4.8 | 1.7 | 58 |
| McArthur River (Glencore), Australia | 151.6 | 4.1 | 6.3 | 49 |

a little molybdenite [$MoS_2$]. Characteristic gangue minerals include magnetite [$Fe_3O_4$], specular hematite [$Fe_2O_3$], and such lime-, magnesium-, and iron-bearing silicates as epidote, diopside-hedenbergite, tremolite-actinolite, garnet (andradite and grossularite), chlorite, biotite, wollastonite, and vesuvianite (Bushell et al. 1985).

Many other minerals, both sulfides and gangues, are of local occurrence in lead–zinc deposits but may be prominent in certain ore bodies. The mineral proportions and associations depend on the type of ore deposit that is formed under the varying geologic conditions imposed by the nature of the country rock, its structure, its temperature and pressure at the time of mineral deposition, and the source and composition of the ore-depositing solutions. Certain mineral associations recur regularly enough to be recognizable as distinct classes of ore deposits, such as the massive sulfide deposits in schists or metavolcanic rocks wherein sphalerite is associated with chalcopyrite and pyrite or pyrrhotite, with little or no galena or earthy gangues.

Lead ores have been found in every continent and are at currently mined in more than 40 countries. The range of ore grades exploited is normally between 2% and 10% Pb, but it also can fall to well under 1% where lead is a minor by-product. The majority of these mines are underground mines. Lead mines are typically classified into four groups of lead-producing ores, depending on the relative quantities of metal. These are lead ores, lead–zinc ores, zinc ores, and any other lead-containing ores. Whether lead is considered as a main product or by-product is dependent both on geological and economic criteria. Since lead is exploited commonly together with zinc, it is striking that the ratio between both mined metals has altered significantly. In 1960, the ratio of lead to zinc in global mine output was close to 0.7:1. This ratio decreased to 0.3:1 by 2003 and fluctuated only in a narrow range until 2010. Since then it was modestly increasing to close to 0.4:1 by the end of 2014. In the near term, the lead/zinc ratio is expected to increase further with the closure of the very large Century mine in 2016.

Global mine production of lead was about 5.364 Mt in 2014 (Figure 1), with production increases in Australia, China, Russia, and India. Taken together, the ten top mining operations, as illustrated in Table 1, accounted for almost 25% of the total lead in ore production in 2014. As shown in the table, reserves of lead are concentrated in Australia, China, Russia, Peru, Mexico, and the United States. Together these countries account for more than 85% of total reserves. This percentage may be overstated with the dynamic in determining reserve data and given the tendency in many developing countries to calculate reserves only at the time of mining development, which is done to meet business needs. Identified world lead resources total more than 2 billion metric tons. In recent years, significant lead resources have been demonstrated in association with zinc and/or silver or copper deposits in Australia, China, Ireland, Mexico, Peru, Portugal, Russia, and the United States (Alaska). Since most lead-bearing ores are complex and contain a range of metals, selective flotation is needed to permit the separation and recovery of the valuable elements.

### *Mineral Processing Methods*

Although there have been many recent developments aimed at improving the efficiency of production and tackling ore-body problems, basic lead mining methods have been essentially unchanged. Where the deposit allows, open pit mining is carried out. However, very few lead deposits are exploited that way, and the percentage of current world lead open pit mine production is less than 10%, while a number of these mines have parallel underground mining activities. Underground mining is, by far, the dominant mining method for most of world's lead deposits. All ores require some sort of treatment. This process involves concentrating the ore by eliminating the gangue and waste material and, where required, the separation of valuable components in the mineral ore. The ore concentration makes use of the differences in physical properties between the various parts of the ore and typically consists of crushing, a pre-concentration at coarse size if possible, grinding and classification, and concentration.

**Crushing.** The ore, which may include some custom material, is usually crushed and physically broken down into small particles in stages. Some crushing, particularly the first stage, is often done at the mine, the remainder in the concentrator. The sizing of run-of-mine ore depends on ore type and mining procedures, and crushing practice is correspondingly affected.

**Pre-concentration at coarse sizes.** Most lead ore concentration is accomplished by flotation after fine grinding to achieve liberation. However, in some cases, an applied sink–float process rejects a discardable light fraction on crushed but unground ore, resulting in savings in subsequent processing.

Ferrosilicon medium is used in the majority of plants, with galena medium in some. Ferrosilicon is generally considered

Table 2 Reagents commonly used in lead and copper–lead flotation

| Collectors | pH Modifiers | Zinc and Iron Depressants | Frothers | Others |
|---|---|---|---|---|
| Xanthates (ethyl, propyl, isopropyl, butyl amyl), Aerofloat promoters (alkali dialkyl dithio phosphates sometimes with frother), Minerec A | Lime, soda ash, sodium hydroxide, sulfuric acid, crude dry lake products like tequesquite | Sodium or calcium cyanide, zinc sulfate, sulfur dioxide or sodium bisulfite, zinc hydrosulfite | Dowfroth, cresylic acid, pine oil, MIBC (methyl isobutyl carbinol), coal tar, TEB (triethyloxybutane) | Sodium silicate |

Source: Bushell and Testut 1985

to be a superior medium, but galena offers a cost advantage when indigenous. Fines must be separated from the ore by screening and washing before sink–float. The normal range of treated ores for sink–float feed is of the general order of 50 to 6 mm but in one application goes down to 0.5 mm. Jigs are sometimes used on fines to complement heavy media separation. Sink–float is not widely used. Even when a low-grade float can be produced, some of the values may be recoverable by fine grinding and flotation. The economics vary with each situation.

**Grinding and classification.** Crushed ore, after pre-concentration at coarse sizes if practiced, becomes the feed for grinding. If the ore is easy flowing, it may be crushed with cone crushers down to about 3 mm, which will be the feed to ball milling. Otherwise, the crushed ore is further reduced in rod mills or rolls (after pre-concentration, if practiced). Flotation feed is ground in ball mills often in one stage, sometimes in two or three stages, and sometimes with more complicated flow sheets for separate treatment of different ores or lead flotation ahead of final grinding. For lead ores, a reduction to under 0.15 mm is required. In most of the recent mills, cyclones, occasionally in two stages, are used as classifiers in grinding circuits, and in some older mills, rake and/or spiral classifiers have been replaced by cyclones. In most modern plants, the ore is ground to the coarsest size that will permit suitably low rougher tailings losses. Regrind circuits for intermediate products such as the rougher concentrate, cleaner tailings, or a scavenger product must then be employed. This procedure is followed both to minimize grinding costs and to prevent sliming, particularly of galena. Otherwise, middlings are returned to primary grinding. The overflows stay in their respective circuits.

**Concentration.** Most lead ores are fine grained (<0.15 mm) and are concentrated mainly by froth flotation. Flotation results are affected by (1) degree of oxidation, (2) abundance in nature of iron sulfides, (3) presence of copper minerals, and (4) nature of a non-sulfide gangue. If necessary, separate streams may be provided for different ore types. Makeup water is normally fresh water but seawater can be used.

**Sulfide concentration.** The lead mineral is galena, PbS, with a specific gravity of 7.5. Coarse-grained ores are sometimes treated by gravity concentration, but a flotation section is usually justified for the treatment of slimes and reground middlings. Straight flotation is the most common practice. The use of jigs in combination with flotation is employed in some plants. Reagents used in lead and copper–lead flotation are shown in Table 2. In addition, various other reagents are sometimes used as a result of local customs or unusual features of the ore. The optimum reagent balance must be found by experimenting on each ore.

With lead–zinc ores, lead (and copper, if present) are floated before zinc. Lead and copper are usually floated and cleaned together, but sometimes a copper concentrate is floated first. Occasionally a pre-float removes “natural floaters” such as talc or graphite that would otherwise contaminate the lead concentrate.

The amounts of pyrite, marcasite, and pyrrhotite greatly affect flotation and make the differentiation of lead and zinc more difficult. When galena and sphalerite-marrnatite are the principal sulfides, the zinc minerals are substantially inactivated and lead can be floated without depressant or only a little cyanide and with no or little alkali. When iron sulfides are present, lime must be used; cyanide, often with zinc sulfate, is used to depress zinc; and sulfites are occasionally added to depress iron. Lead flotation is generally at a pH in the range of 7.5 to 10, with the pH in the cleaners sometimes higher than in the roughers. The addition of lime to the cleaners without further addition of xanthate increases the xanthate concentration in solution. The consequent desorption of collector depresses marginally floatable particles to the tailings. If the ore contains reactive pyrrhotite, the pH should not exceed 11.2, as more alkaline solutions will liberate sulfide ions to solution and affect flotation adversely. The number of cleaning stages required varies; one or two are often sufficient, but complex ores such as Brunswick (Canada), Sullivan, and others employ more. Sometimes lead rougher tailings are re-floated to produce a scavenger concentrate that is generally recycled to the roughers, often after a regrind. Lead cleaner tailings might also be reground before recycling to the roughers. Flotation times in lead flotation are noted in some individual concentrators; 10–20 minutes is typical in roughing.

The bulk lead–copper concentrate is cleaned to the optimum grade and then is split into separate lead and copper concentrates. Since these are both usually end products, the need to achieve optimum grade in the bulk concentrate is obvious (sometimes the lead product is further concentrated). Two orders of lead–copper separation are used. In one, the lead is floated while the copper is depressed, and in the other, the copper is floated while the lead is depressed. When lead is floated, the copper is depressed with cyanide. Cyanide loses its effectiveness readily, particularly in the presence of cyanide-consuming constituents in the ore, so the reagent is generally stage added. Cyanide depression of copper minerals is pH sensitive, so pH should be controlled closely. The optimum range varies with individual concentrators but usually is between 10.0 and 11.5. When copper is floated, lead is depressed through use of sodium dichromate, sulfur dioxide, or starch while additional collector such as Z-200 and frother are added as required. Examples for alternative (but not common) lead concentration is the depression of copper with an ammoniated zinc cyanide complex and the addition of activated carbon to adsorb excess bulk flotation reagents. Another concentration method for a copper–lead concentrate is conditioning with a guar-dextrine depressant for separation

**Table 3 Reagents commonly used in oxidized lead flotation**

| Collectors | pH Modifiers | Zinc Depressants | Sulfidizing Agents | Frothers | Others |
|---|---|---|---|---|---|
| Xanthates | Sodium carbonate | Sodium cyanide | Sodium sulfide | Pine oil | Sodium silicate |
| Amylxanthates | Sodium hydroxide | Zinc sulfate | Sodium sulfhydrate | Cresylic and xylenic acids | Oil |
| Thiocarbamates | | Sodium sulfide | | Dowfroth | Creosotes |
| Mercaptobenzothiazol | | | | Speld 1333 | Coal tar |
| Long-chain thioalkyl acids | | | | Aerofroth 65 | Carboxymethyl cellulose |
| Aerofloat | | | | | Kerosene |
| Oleic acid | | | | | Lignosulfonates |
| Refined tall oil | | | | | |
| Reagent 404 | | | | | |

Source: Bushell and Testut 1985

and then conditioning with sulfur dioxide at pH 4.5. Copper concentrate is floated with Z-200 and cleaned three times. The copper separation tailing is floated with xanthates at pH 5.8–6.0 to concentrate lead and depress pyrite and sphalerite. The lead concentrate is cleaned three times. Alternatively, the copper–lead separation can be accomplished with sulfur dioxide and sodium dichromate at pH 5.2 to depress galena.

Sometimes appreciable zinc reports to the lead concentrate from the final stage of normal cleaning and needs to be removed. This zinc apparently floats with the lead because of activation by lead or copper ions. "Dezincing" is analogous to lead–copper separations in that the lead concentrate is separated into two end products—a final lead concentrate and a zinc concentrate, which is added to the zinc concentrate obtained by normal zinc flotation. This practice is followed at the Sullivan mine where the material transferred contains about 15% Pb and 44% Zn. The economic desirability of this transfer follows directly from the economic considerations of separating within reasonable limits; lead in zinc concentrates going to the Teck Metals smelter is preferable to zinc in lead concentrates. In this process, the lead recleaner concentrate is heated to 38°C and conditioned at pH 11.6 with added copper sulfate. In theory, this process removes the xanthate from the lead, allowing it to be absorbed by the activated zinc. Desorption of xanthate depresses lead to the tailings, which become the final lead concentrate, and the concentrate (zinc) is added to the final zinc concentrate.

At other lead–zinc mines, the first-stage flotation concentrate, containing both lead and zinc, is refloated with activated carbon, caustic soda, maize starch, and sodium dichromate to yield tailings that become part of the final lead concentrate and a float that goes to the low-grade zinc circuit. If the feed is partly oxidized, a bulk float is first made and then separated into lead, zinc, and iron concentrates.

**Oxidized lead ores.** The lead minerals considered first are cerussite ($PbCO_3$) and anglesite ($PbSO_4$). Both are soft minerals that usually slime badly during comminution.

Cerussite ores are floated with a powerful sulfide collector after the cerussite has been sulfidized. Cerussite usually sulfidizes readily. Sodium sulfide is often used. However, if a large amount of sulfidizing agent is required, a mixture of sodium sulfide and sodium hydrosulfide may be preferred in order not to increase the pH too much. A succession of flotation steps is sometimes used, each step comprising a quick sulfidizing reaction, followed by flotation. With inefficient conditioning, sodium sulfide consumption is sometimes reported to be very high. Slime gangue dispersion by sodium silicate is usual. The sodium silicate is often added with the sodium sulfide or a mixture of sodium sulfide and sodium sulfate. After conditioning, the pH has to be generally close to 8.5 for good flotation. The conditioning time is critical. When the temperature rises, conditioning time must be shortened. Alternatively, sodium carbonate may be added to slow down and control the sulfidizing action in the conditioner. Aeration in the conditioner is also helpful. The conditioning time then is not so critical and the floatability of the sulfidized cerussite lasts longer after conditioning. A table of widely used reagents are listed in Table 3. Potassium amylxanthate and Reagent 404 are often used as collectors. On some ores, Reagent 404 (either alone or mixed with a xanthate or an Aerofloat collector) has given good results without sulfidizing. An insoluble oil (a creosote, coal tar, or oil–xylenol mixture) is often used to reinforce the soluble collector action. It can be added with advantage as an emulsion with the frother. The combination speeds up flotation in both roughing and cleaning stages and the soluble collector consumption is decreased. Two or three cleaning stages are usual. Conditioning time is in the range of 2 to 3 minutes and flotation time is 15–45 minutes in roughing.

Anglesite is more difficult to float by sulfidizing than cerussite, and the permissible pH range is narrower. The sliming tendency of oxidized lead ores is a source of difficulties with long chain collectors. However, where the gangue is acid, fatty acids are sometimes used as collecting agents. Flotation with fatty acids loses selectivity in the presence of limestone or dolomite.

Pyromorphite, $Pb_5(PO_4)_3Cl$, and mimetite, $Pb_5(AsO_4)_3Cl$, are the extremes of an isomorphous series, mimetite being less abundant than pyromorphite. They are generally finely disseminated and associated with cerussite and anglesite. They can be concentrated by flotation. Desliming before fine grinding may be necessary to reject the primary slimes.

Two flotation schemes are possible: either a flotation of cerussite and anglesite first after sulfidizing, followed by pyromorphite and mimetite flotation with fatty acids; or all minerals are floated together with fatty acids. Oleic acid and refined tall oil containing 2%–10% resin acids are the preferred collectors. They are used either as soaps or emulsified with nonionic emulsifying agents. Slime and pH control arc obtained with sodium silicate and sodium carbonate. Sulfidizing before fatty acid flotation may be beneficial.

**Lead–zinc ores with both sulfides and oxides.** Oxidized ore with insufficient oxidized minerals to justify separate recovery nevertheless poses special problems in flotation. With straight lead–zinc ores, much of the trouble results from activation of zinc and possibly iron sulfides by lead ions coming from oxidized lead minerals. Washing the ore before grinding can be helpful. Cyanide is useless for overcoming lead activation, but addition of soda ash or lime to the grinding circuit can be helpful.

Mixed sulfide–oxide ores with basic gangue can sometimes be treated for recovery of oxidized minerals as well as sulfides. Effective depression of sphalerite, which has been activated by lead ions, is essential. Sodium sulfite and bisulfite, zinc sulfate combined with ammonium sulfate, zinc sulfate and sodium silicate, or reagents that precipitate lead ions like sodium sulfide and zinc powder are used. However, sodium sulfide sometimes depresses sphalerite permanently.

Flotation of ores without iron sulfides may be conducted in either of two sequences, galena-sphalerite-cerussite or galena-cerussite-sphalerite. If smithsonite is present, it is floated last after desliming. With the order galena-sphalerite-cerussite, flotation is usually conducted in a neutral circuit. To depress sphalerite, zinc sulfate has to be used sparingly, otherwise the consumption of sulfidizing agent in the cerussite circuit would be increased. Sphalerite is floated with minimum copper sulfate, as an excess can harm cerussite flotation. Cerussite is floated after sulfidizing with sodium sulfide or sodium sulfide plus sodium hydrosulfide. Sodium silicate is nearly always essential. With the flotation order galena-cerussite-sphalerite, or if galena and cerussite are floated together, the difficulty is to avoid permanent depression by sodium sulfide. Another adverse effect of sodium sulfide is that it is sometimes adsorbed by gangue minerals that later float after activation by copper sulfate. Potential remedies include addition of ferrous sulfate, which can precipitate the soluble sulfide, or the pulp can be thickened and the water rejected. Desliming the pulp is more effective, but it entails losses of fine sphalerite.

When mixed oxide–sulfide ores contain iron sulfides, flotation is complicated further. The classic flotation sequence is galena-sphalerite-pyrite-cerussite-smithsonite. If smithsonite is not recovered and pyrite flotation is not justified, a simpler two-circuit scheme—galena plus cerussite-sphalerite—is preferred, if it works. Pyrite is usually depressed with cyanide and lime (Doyle 1970).

## Lead Concentrates: Extraction Processes and Schedules

The three major factors determining revenue from ores and concentrates produced are the prevailing prices for refined lead metal, freight to the purchaser's location, and the schedules under which the materials are purchased.

Lead metal prices have, by far, the greatest impact on the price negotiable for the corresponding concentrates, since in all smelter schedules, payments for contained metal values are based on current metal price. In general, the operating margin and profit potential available to the smelter through the common schedule have been small, although a cost is added to treatment charge for emission control cost.

Under its schedule of purchase, the price offered by a smelter for an acceptable raw material is dependent on several factors. These include the specific smelting and subsequent refining processes, the limitations of a given plant in flexibility, state of repair and proximity to metal markets, and the normal metallurgical practice and costs that relate to production targets and the type of raw material input. Each concentrate has a unique specification, based both on its lead content and the type and relative quantities of recoverable and penalty elements that it contains. Lead concentrates vary from about 30% to 80% of contained lead. The quality of concentrates is also very different, ranging from clean, pure concentrates to highly complex and impure concentrates. The latter materials can be either more valuable by having a high precious metals content or can contain significantly more deleterious impurities that are subject to a penalty.

In addition, the combination of environmental concerns, the actual trend of increasing recycling rate, the rather stagnating net lead mine output, and an increase in smelter capacity as a result of growing lead demand means that many smelters have been forced to alter their feed mix to include a greater share of secondary materials. Today, only 80% of the lead produced by primary smelters is from lead and/or bulk concentrates, down from more than 90% two decades ago.

### *Primary Lead Smelter Schedules*

**Payments.** In complex concentrates, primary lead smelters typically offer payment for most of contained lead, silver, gold, and copper, and sometimes for minor metals such as zinc, bismuth, antimony, and platinum, if recovered. Very infrequently, payment may be offered for other metal values. Only a part of the contained value will be paid for, the remainder representing the expected process loss. The price applicable will be somewhat below the market price of metal to allow for refining, shipping, and sales costs borne by the smelter. The precise formula varies from schedule to schedule, but these provisions are always contained. Very often, no payment will be offered for minor metal values that the smelter can and does recover. Both the list of recoverable metals and the recovery attainable are related to the smelting process and plant, and to the composition of the charge.

**Penalties and bonuses.** A penalty or bonus for a raw material constituent is a compensation for its effect in the smelter operation on recovery of metal values and incurred costs. These may be specified directly in amount and level of application but frequently are calculated as an adjustment to treatment charge. Common impurities in lead concentrates are bismuth, arsenic, antimony, cadmium, mercury, iron, and halides. These impurities cause the lead smelters the greatest problems during processing and are designated penalty elements. Excessive moisture content and additional handling costs related to shipment size or screen size are also usually compensated in this way.

**Treatment charge.** This is a deduction from the gross payment for values designed to cover all smelting operation costs, overhead, and depreciation, and allow for profit. It usually takes the form of a fixed deduction per dry ton of material processed, and thus its impact is greater on lower-grade materials. A minimum treatment charge per lot is specified. Some smelters determine the treatment charge with reference to the total payment for main metal values. This formula relates it to metal price as well as to grade. As smelting costs rise, with emission control a major contributor, the increase will be reflected by higher treatment charges (Rich 1994).

### *Primary Lead Smelting Processes*

The recovery of lead from concentrates and other raw materials is carried out almost exclusively through pyrometallurgical processes due to the insolubility of many lead compounds in water and most common acidic solution. Smelting of most primary lead from sulfide materials is based on the roast reduction process. The conventional process included two main steps. The first stage consisted of roasting and sintering of lead sulfide and fluxes on an updraft sinter machine to produce lead oxide sinter, which is followed by a reduction process in a blast furnace. The latter can be a traditional shaft furnace or an Imperial Smelting type. Other technologies include electric furnaces or rotary furnaces. Lead oxide raw materials are smelted directly under a reducing atmosphere. The residual lead from the produced slag can be further reduced through a subsequent fuming step. Figure 3 depicts the main reactions taking place at the various stages of lead production (Stephens 2010).

About 50% of the installed capacity is still producing lead using Dwight-Lloyd updraft sinter machine and blast furnace operations, which was introduced at the beginning of the 1900s. This old practice experiences more and more difficulties regarding compatibility with today's requirements in respect to efficiency and environmental protection. Therefore, extensive research studies have been performed in different parts of the world since the beginning of the 1970s, resulting in the development of several new technologies for primary lead smelting. Most of these processes were based on direct and mainly continuous smelting technologies, but only some, like the TSL (top submerged lance), QSL (Queneau–Schuhmann–Lurgi), SKS (Shuikoushan), Kivcet, and Kaldo processes, have been realized on an industrial scale. The commercial implementation of these novel technologies toward the end of the 20th century successfully challenged the conventional method of lead smelting, and most of them have proven to be economically and environmentally viable. The intensification of the metallurgical reaction by applying the bath or flash smelting principle in conjunction with oxygen use resulted in cost savings and a higher flexibility with respect to raw materials and additives usage. By synchronizing individual auxiliary plant sections with the smelting process, a virtually waste-free production and low-emission mode of operation with optimum energy exploitation is achieved (Siegmund 2000a, 2000b).

**Conventional technology (sinter machine–blast furnace).** The conventional process consists of the two steps of sinter roasting and reduction. Both process steps are carried out in independent aggregates. A typical process block diagram of a sinter machine–blast furnace plant is shown in Figure 4.

The objective of the sinter roasting process is to oxidize virtually the entire amount of prevailing lead sulfides to lead oxide and convert the concentrate into an agglomerated feed with suitable mechanical properties (mainly size, hardness, and porosity) and chemistry requirements for the subsequent reduction step in the blast furnace. This sintering of the concentrates is accomplished by adequate addition and mixing with lime-, silica- and iron-containing materials as fluxes and return of sintering fines. The solid–gas reactions during the oxidizing roast of lead concentrates is more complex than for other nonferrous metals. The roasting reaction forms lead sulfate, which itself reacts with still available lead sulfide to form lead sulfates/oxide compounds. Therefore, the sequence of the roasting reactions can be assumed to be $PbS \rightarrow PbSO_4 \rightarrow PbSO_4 * PbO \rightarrow PbSO_4 * 2PbO \rightarrow PbSO_4 * 4PbO \rightarrow PbO$. In addition, the sinter process is hampered by the formation of low-melting-point eutectic compounds such as $PbS\text{-}Sb_2S_3$ (426°C), $PbS\text{-}Cu_2S$ (540°C), and $PbO\text{-}SiO_2$ (714°C). Another reason is the higher combustion heat availability from such concentrates, which could cause fusing of the sinter charge without added, and costly, recirculation of sinter.

**SMELTING**

**Oxidation of Sulfides**

$PbS + 1{,}5O_2(g) \rightarrow PbO + SO_2(g)$ **(EQ 1)**

$ZnS + 1{,}5O_2(g) \rightarrow ZnO + SO_2(g)$ **(EQ 2)**

$FeS + 1.5O_2(g) \rightarrow FeO + SO_2(g)$ **(EQ 3)**

$FeS_2 + 2.5O_2(g) \rightarrow FeO + 2SO_2(g)$ **(EQ 4)**

**Decomposition of Sulfates and Ferrites**

$PbSO_4 \rightarrow PbO + SO_2(g) + 0.5O_2(g)$ **(EQ 5)**

$ZnSO_4 \rightarrow ZnO + SO_2(g) + 0.5O_2(g)$ **(EQ 6)**

$ZnFe_2O_4 \rightarrow ZnO + Fe_2O_3$ **(EQ 7)**

**Formation and Oxidation of Metallic Lead**

$PbS + 2PbO \rightarrow 3Pb + SO_2(g)$ **(EQ 8)**

$Pb + 0.5O_2(g) \rightarrow PbO$ **(EQ 9)**

**Equilibrium with Ferric Iron**

$PbO + 2FeO \rightarrow Pb + Fe_2O_3$ **(EQ 10)**

**Fuel Combustion**

$C + O_2(g) \rightarrow CO_2(g)$ **(EQ 11)**

$C + 0.5O_2(g) \rightarrow CO(g)$ **(EQ 12)**

**REDUCTION AND SLAG FUMING**

$PbO + C \rightarrow Pb + CO(g)$ **(EQ 13)**

$PbO + 0.5C \rightarrow Pb + 0.5CO_2(g)$ **(EQ 14)**

$PbO + CO(g) \rightarrow Pb + CO_2(g)$ **(EQ 15)**

$ZnO + CO(g) \rightarrow Zn(g) + CO_2(g)$ **(EQ 16)**

$Fe_2O_3 + C \rightarrow 2FeO + CO(g)$ **(EQ 17)**

$Fe_2O_3 + CO(g) \rightarrow 2FeO + CO_2(g)$ **(EQ 18)**

$C + CO_2(g) \rightarrow 2CO(g)$ **(EQ 19)**

**AFTERBURNING AND SULFATION**

$Zn(g) + 0.5O_2(g) \rightarrow ZnO$ **(EQ 20)**

$Pb(g) + 0.5O_2(g) \rightarrow PbO(g)$ **(EQ 21)**

$PbO(g) \rightarrow PbO(l)$ **(EQ 22)**

$PbO(g) + SO_2(g) + 0.5O_2(g) \rightarrow PbSO_4$ **(EQ 23)**

$ZnO + SO_2(g) + 0.5O_2(g) \rightarrow ZnSO_4$ **(EQ 24)**

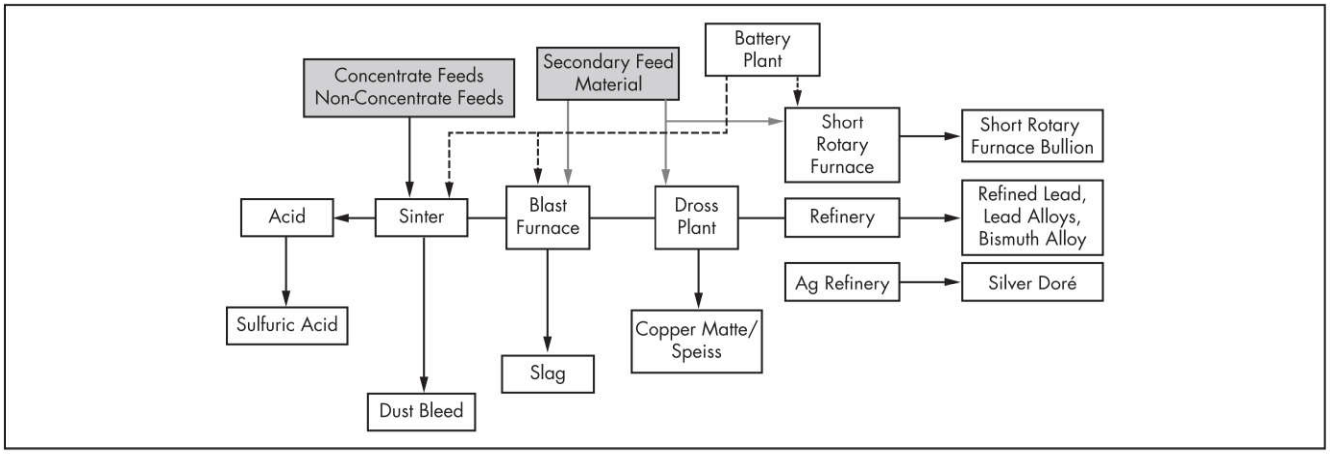
$CO(g) + 0.5O_2(g) \rightarrow CO_2(g)$ **(EQ 25)**

Note: The chemistry of all the direct lead smelting processes are similar but differ slightly in the temperatures or oxygen potentials used.

Source: Stephens 2010

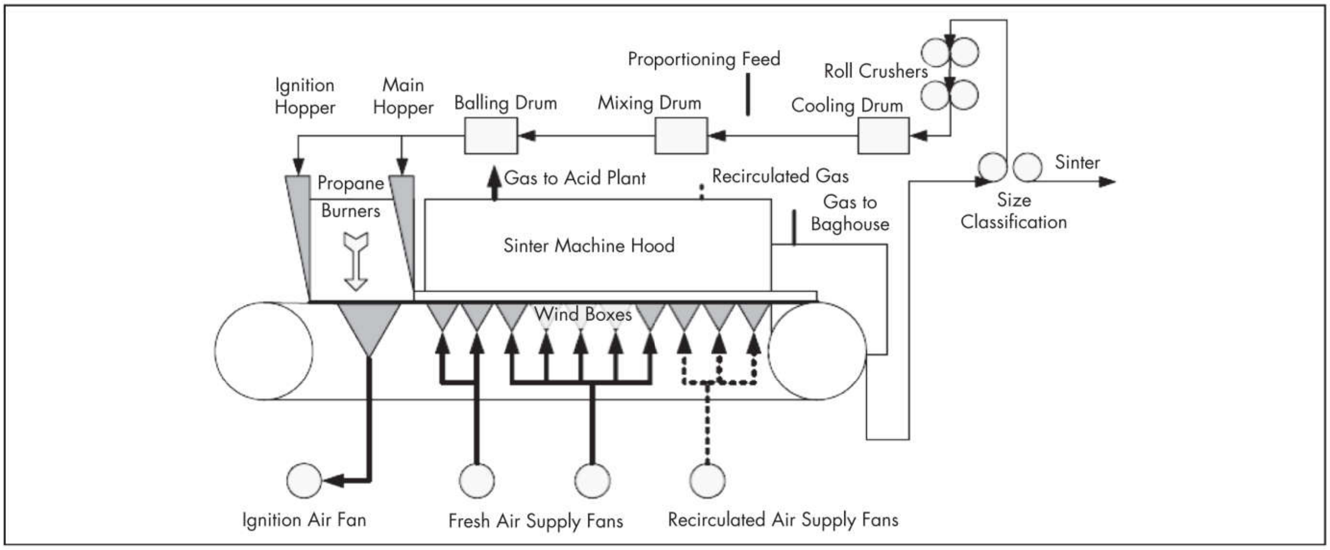
**Figure 3 Main chemical reactions during the recovery of lead at various production stages**

Sintering of lead blast furnace feed can be performed either on updraft or downdraft machines. For the sinter roasting process, usually an updraft Dwight-Lloyd sinter machine, as depicted in Figure 5, is preferred for many reasons. Downdraft sinter plants are generally less able to handle the contained sulfur in lead concentrates in an ecologically acceptable way and are therefore more likely to reject higher-sulfur concentrates, notably pyritic concentrates. Dwight-Lloyd sinter machines consist of a continuous system of pallets with a grate bottom, which convey the feed mix through the machine. After a thin layer of feed material (40–60 mm) has been ignited, the main amount of feed material is added, forming a sinter bed, which then enters the



Adapted from Jiao 2010

**Figure 4 Typical process block diagram of a sinter machine–blast furnace operation**



Adapted from Jiao 2010

**Figure 5 Updraft sinter machine**

main reaction chamber. Here, air is pushed upward through the permeable charge driving the main reaction layer from the bottom of the sinter bed to the top. At the end of the sinter process, about 10% of the lead is already present in metallic form. The high temperatures in the reaction layer aid in the agglomeration process of the feed particles. After discharge from the sinter machine, the sinter is crushed and screened. Sinter with the appropriate size is fed to the blast furnace operation while fines are returned to the sinter machine. During the oxidation process on the sinter machine, sulfur dioxide is generated that must be recovered. Most operations convert the sulfur dioxide into sulfuric acid. The advantages of this operating mode include no metallic lead lost by dripping into the wind boxes, high specific sintering capacities, the ability to efficiently separate gases and produce an $SO_2$-containing gas of strength compatible with sulfuric acid production, recirculation of process gases with low-sulfur-dioxide concentrations, minimum wear of the travelling grates, and reduced burden for the blast furnace operation. Typical operating data for sinter machines are shown in Table 4 (Jiao 2010).

The reduction of lead oxide is achieved through reduction smelting in either the more common vertical blast furnace or an Imperial Smelting process (ISP) zinc–lead furnace. Conventional lead blast furnaces normally have a rectangular cross section. The majority of lead blast furnace smelters process lead sulfide concentrates of fairly high grade (>60% Pb) and operate with a fairly constant raw material charge. However, most accept lower-grade lead ores in moderation. More and more plants incorporate zinc plant residues and other secondary lead-bearing materials into the blast furnace charge, operating with high zinc slags from which zinc is subsequently recovered by fuming. Commonly, zinc in slag is held below 12% and there is no subsequent recovery (Young et al. 2010). Capacity increases in existing blast furnaces have recently been accomplished through improvements in the sinter quality (hardness, porosity, size distribution), closed furnace tops, feeders with better charge distribution, preheating,

**Table 4 Selected sinter plant operating data**

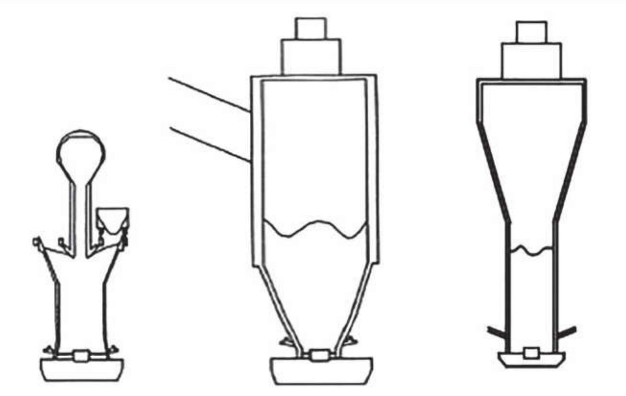
| Item | Brunswick (Canada) | Port Pirie (Australia) | Peñoles (Mexico) | Chigirishima (Japan) |
|---|---|---|---|---|
| Hearth area, $m^2$ | 120 | 83.6 | 120 | 33 |
| Capacity, t/h | 45 | 90 | 60 | 22 |
| Percent of secondary | 42 | 23 | 0 | 20 |
| Feed moisture, % | 6 | 11 | 6 | 4.5 |
| Ignition fuel | Propane | Natural gas | Natural gas | Heavy oil |
| Percent $SO_2$ in exhaust gas | 4.5 | 6 | 5.5 | 6 |
| Sulfur burning rate, $t/m^2/d$ | 1.4 | 2.8 | 1.4 | 1.4 |
| S in sinter, % | 1.5 | 1.5 | 2.5 | 2.5 |

Source: Jiao 2010

and oxygen enrichment of air. Typical schematic drawings of different blast furnace types are shown in Figure 6.

The reduction of the lead oxide sinter is achieved through the addition of recycled intermediates and secondary materials, fluxes, and metallurgical coke. The charge is fed through either an open or a sealed furnace top. Air, or oxygen-enriched air to reduce coke consumption, is blown through tuyeres into the furnace at the bottom of the shaft. The coke from the feed mix is combusted in this area, forming carbon monoxide for lead oxide reduction. This reduction reaction has already started at temperatures of 160°C. Although the direct reduction of lead oxide is limited to the melting and slag zones in the middle and lower part of the furnace, a considerable recirculation rate of evaporated and condensed phases (lead compounds, zinc, and others) are observed as the charge progressively descends in the furnace. The charge transforms into the main components: lead bullion and slag. Depending on the charge composition, matte and speiss can also be formed. Matte is typically formed at sulfur contents above 2% in the charge and contains up to 35% Cu, 10%–25% Pb, up to 15% Fe, up to 8% Zn, 25%–1,200 g/t Ag, and some arsenide. The generated amount of matte may vary between 2.5% and 10% of the charge. Speiss is formed when increased amounts of arsenic, antimony, nickel, and cobalt are contained in the charge. Resulting speiss consists of 30%–40% Cu, 20%–35% Pb, 5%–10% As, up to 10% Sb, 5%–12% Ni, 3%–15% Fe, and 2%–3% S. All products accumulate at the base of the furnace and are continuously tapped into a forehearth. In general, the formation of speiss is not desired since the recovery of precious metals is complex and expensive. Furthermore, the operation of the forehearth is more labor and energy intensive due to the high melting point and density of speiss. Physical separation can be easily achieved here due to the different densities of the products (lead bullion $\approx$ 11 $t/m^3$, matte $\approx$ 5–6 $t/m^3$, speiss $\approx$ 7–8 $t/m^3$, slag <4 $t/m^3$). The temperature in the upper part of the hearth (slag zone) is about 1,200°C and in the lower part (lead zone) about 900°C. Typically, 95%–96% of the lead is recovered in the lead bullion (Longval et al. 2008).

The slag constituents are mainly iron silicate and lime but may contain up to 2% Pb and 10%–22% Zn. FeO in blast furnace slags ranges from 25% to 35% in worldwide practice, depending on related contents of $SiO_2$ (20%–25%), CaO (15%–22%), MgO (1%–4%), $Al_2O_3$ (3%–8%), and ZnO. High zinc slags require more iron, which is often added as a separate ironstone flux. Quite commonly, iron in the charge exceeds the requirement for the most economical slag formulation. In such a case, the additional iron demands more lime and silica flux and more thermal energy, and as a result, the smelter schedule will penalize iron in lead concentrates purchased. Pyritic iron in concentrates is generally unwelcome because of the increased ignition heat it represents and additional sulfur handling necessitated. Typical operating data for lead blast furnaces are shown in Table 5 (Jiao 2010).


A. Lead "thimble top" blast furnace
B. Imperial Smelting blast furnace
C. Modified Imperial Smelting blast furnace for lead smelting

Source: Longval et al. 2008

**Figure 6 Different types of blast furnaces**

**Imperial Smelting process.** The Imperial Smelting process (ISP) technology is a variant of the conventional blast furnace and is designed to recover zinc and lead simultaneously. Lead content is less critical; it regularly processes lead concentrates below 50% Pb content, particularly with appreciable copper content, and mixed (bulk) lead–zinc concentrates of as low as 10% Pb, depending on the zinc content. Usually, lead concentrates are incorporated into the charge. Lead has an important hardening effect on sinter, substituting for silica, which is the practical alternative. $SiO_2$ flux requires compensatory lime flux addition—thus, lead replacing silica makes for lower slag production with benefits in increased fuel efficiency and lower zinc loss. Mixed lead–zinc concentrates of Pb + Zn content as low as 30% have been treated on occasion but presumably in conjunction with higher-grade materials. The process will also handle zinc ash, waelz oxides, and oxidic Pb–Zn ores as charge components. Considerable flexibility is available in charge-compounding, and the zinc blast furnace accepts properly compensated changes in feed blends without difficulty.

Four major process steps make up the ISP technology to produce lead and zinc (Figure 7). As in the blast furnace

**Table 5 Operating data of several lead blast furnaces worldwide**

| Item | Brunswick (Canada) | Port Pirie (Australia) | Peñoles (Mexico) | Chigirishima (Japan) |
|---|---|---|---|---|
| Furnace type | With Imperial Smelting furnace charging | Open top, two-row tuyere | Single-row tuyere | Single-row tuyere |
| Hearth area, $m^2$ | 13.3 | 18.8 | 10.2 | 9.4 |
| Number of tuyeres | 44 | 92 | 42 | 56 |
| Sinter smelted, t/h | 40 | 58 | 19 | 19 |
| Blowing rate, $Nm^3/h$ | 20,000 | 26,000 | 10,000 | 9,000 |
| Oxygen enrichment, % | 27.5 | 27 | 22.5 | 22 |
| Blast preheating | No | No | No | 200°C |
| Coke rate, % | 10.5 | 9.5 | 14 | – |
| Bullion production, t/yr | 84,000 | 230,000 | 59,000 | 64,000 |
| Pb in slag, % | 1.2 | 2.3 | 1.5 | 2.8 |

Source: Jiao 2010

process, sintering is conducted in a Dwight-Lloyd machine. The feed mix consists of complex lead–zinc concentrates, zinc-rich residues and dusts, recirculated drosses, limestone, silica fluxes, and returned sinter fines. The produced sinter containing ~15%–22% Pb as well as 42%–45% Zn is screened and mixed with secondary zinc materials and coke preheated to 800°C. The lead and zinc is reduced through the injection of preheated air to metal. Zinc is produced as vapor, which is then condensed in a spray of molten lead. Liquid zinc separates on cooling and is either sold directly or refined. As in a blast furnace, lead collects in the hearth together with molten slag and is tapped. The solvent action of metallic lead makes it possible to recover therein the silver, gold, and bismuth content of concentrates together with a substantial part of the copper. The process cannot be confined to zinc recovery alone. Some lead in the charge is necessary for recovery of minor values as well as for reasons of economy in sintering and furnacing.

Because of the lack of raw materials and for economic reasons, many Imperial Smelting furnace plants have been permanently closed down or converted to a pure lead blast furnace. Today, only nine plants are still in operation: five in China, two in Japan, one in India, and one in Poland (Fallas 2010).

### *Modern Applied Technologies*

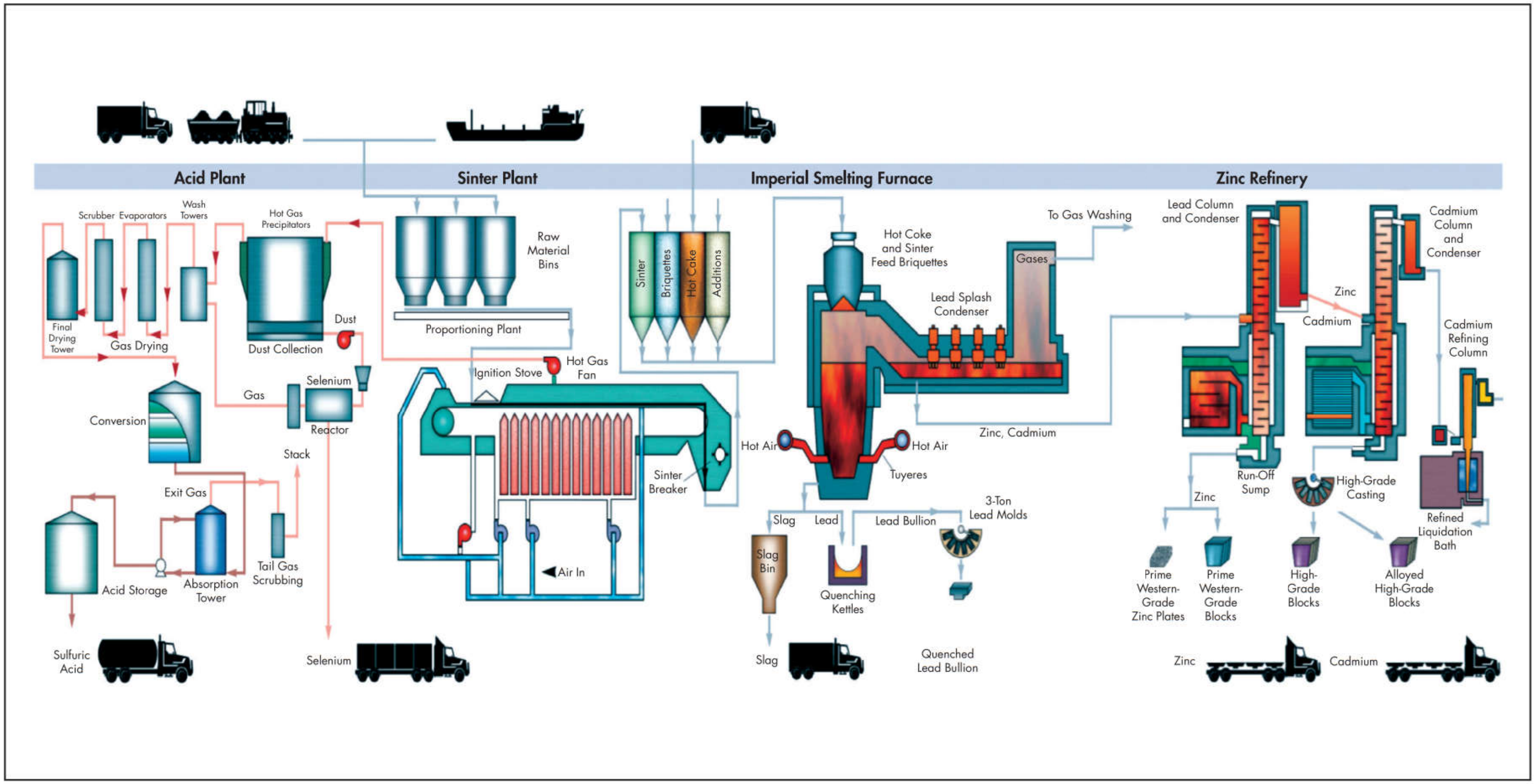
**Kivcet smelting technology.** The technology of the Kivcet process employs the principles of simultaneous flash smelting of lead-bearing materials using technically pure oxygen. In conjunction with electrical energy, carbon reduces the lead oxide in the slag. The process was developed by Vniitsvetmet in Ust-Kamenogorsk, Kazakhstan, and transferred into industrial scale.

Today, two smelters are operating based on the Kivcet technology. The first commercial-scale smelter was constructed for Enirisorse (now Glencore) at Portovesme, Sardinia. The smelter was commissioned in 1987, and its current annual production capacity is 100,000 t/yr Pb, predominantly based on treating materials from primary sources. The second smelter was built at Teck Metals in Trail, Canada, and started operations in 1997. The annual capacity of the Trail smelter is up to 120,000 t/yr Pb. To meet the needs of Trail Operations as an integrated zinc–lead smelter, the smelter is designed to treat a high-residue charge. Metal and co-product recoveries are maximized along with reduced energy and labor costs and reduced environmental impact (Rioux et al. 2008).

A simplified flow sheet of the Teck Metals smelter is shown in Figure 8. The Kivcet process is able to treat a wide variety of lead-bearing raw material. At the Portovesme plant, the treated ratio of primary to secondary materials is about 3.5:1, while it is 1:2 at Teck Metals. The majority of the Teck Metals raw material consumption consists of internally generated zinc plant iron residues plus lead concentrates and precious metal concentrates as well as battery scrap. The flash smelting process requires drying of the feed material to <1% moisture content prior to being charged into the furnace. The exiting dry product is conveyed from the drying furnace into a ball mill, grinding it to –1 mm.

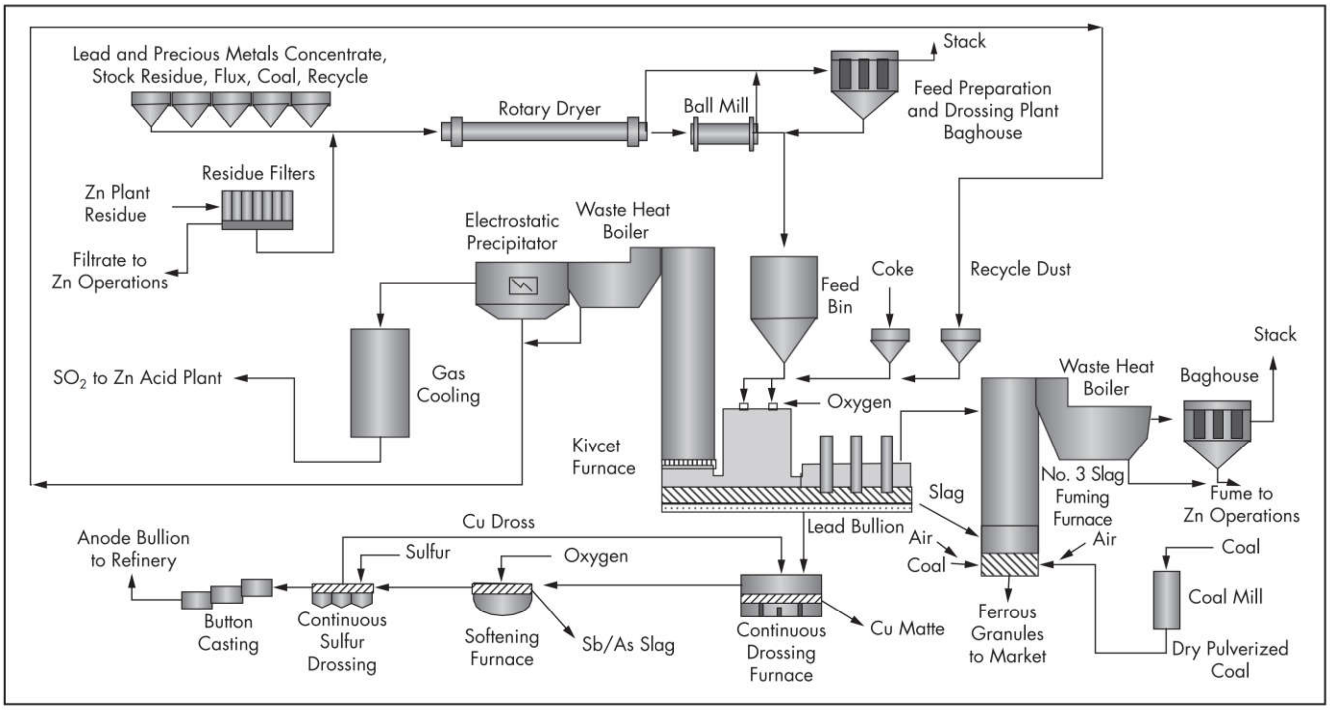
The Kivcet furnace mainly consists of three primary areas: a smelting shaft, an adjoining electric furnace that is separated by a water-cooled partition wall, and the uptake shaft (Figure 9). Concentrate burners at the top of the reaction shaft (four at Teck Metals, two in Portovesme) serve to mix the pre-dried feed material with oxygen to spontaneously initiate the roasting and smelting reactions as the charge travels down the reaction shaft. The reaction shaft is made entirely of water-cooled copper tubes cast in copper elements from the centerline of the air-cooled hearth. The reaction shaft is also equipped with a natural gas auxiliary burner (12,000 Mcal/h at Teck Metals) for heat during feed interruptions. The feed-to-oxygen weight ratio is crucial for the control of the desired reducing condition in the flame. An abundance of oxygen will increase the lead content in the slag and tend to form magnetite deposits under the reaction shaft, whereas an oxygen deficiency will result in unburned feed and formation of a matte phase and sulfide deposits in the uptake shaft. Moreover, a rather erratic and varying feed composition is detrimental to the process, making it extremely difficult to achieve stable operating conditions. Fluctuations in the fixed carbon content of the fuel coal should be minimized. The implementation of a residue-blending device and storage bins for flue dust with loss-in-weight discharge are required to avoid poor blending of different residues and variations in the amount of recirculated flue dust.

The flame temperatures are monitored frequently under each concentrate burner and are used to adjust the feed calorific value. Flame temperatures lower than 1,380°C indicate that the charge is under-fueled. Flame temperatures higher than 1,420°C indicate an excess of coal in the charge. Smelt samples taken under each burner are analyzed for sulfur. The goal for typical residual sulfur remaining in the smelt



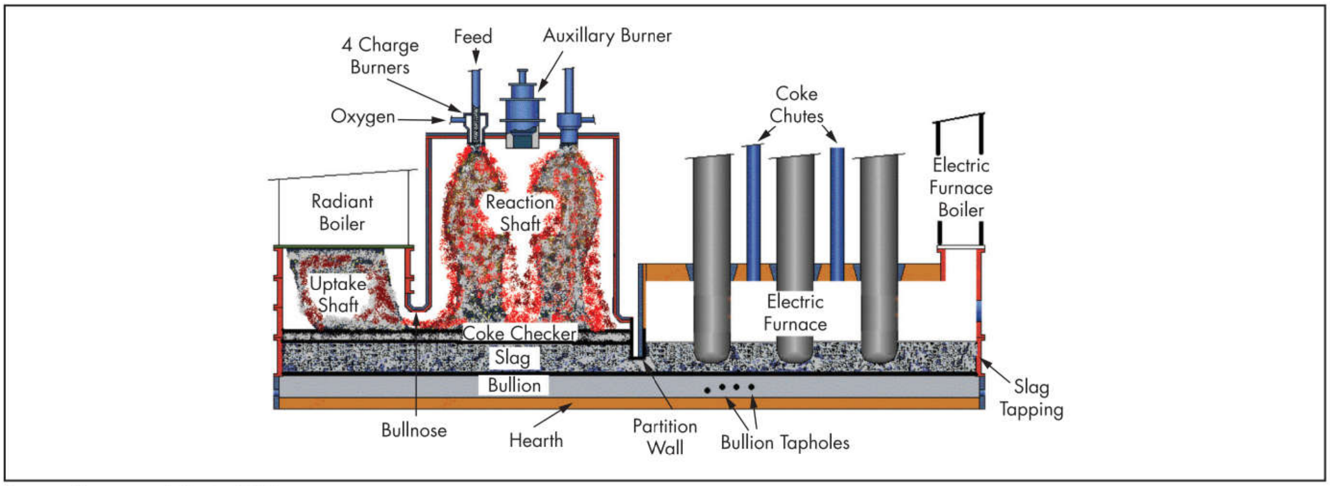
Source: Fallas 2010

**Figure 7 ISP process flow sheet**



Source: Ashman et al. 2000. Copyright 2000 by The Minerals, Metals & Materials Society. Used with permission.

**Figure 8 Flow sheet of the Teck Metals lead smelter**



Source: Goosen and Martin 2000

**Figure 9 Cross section of Kivcet furnace**

are 0.5%–1.2%. Coarser coke (5–15 mm) enters the furnace together with the charge to float on the slag layer in the reaction shaft area forming a "coke checker." The added coke rate is adjusted to maintain a coke layer of ~100–150 mm thick to efficiently reduce the generated lead oxide as the smelt flows through the coke. One control parameter of the coke-layer thickness is maintaining the temperature of the coke checker between 1,100°C and 1,200°C. Coke checker temperatures higher than 1,200°C indicate a thin layer of coke in the furnace; temperatures lower than 1,100°C mean a thick layer of coke or coke piling. Poor coke checker performance may result in accretion formation because of operation with a more reducing flame to lower the lead content in the slag. These accretions mainly consist of lead sulfide. They can grow so large that they start blocking the gas passage at the bullnose (Figure 9). The bullnose accretion condition is monitored by measuring the draft differential between the reaction shaft and the boiler on a continuous basis. Accretion management and the directly dependent performance of the coke checker is one of the most critical control parameters to the entire operation.

The molten and virtually reduced slag flows under a submerged water-cooled copper partition wall, which separates the electric furnace (55 $m^2$ at Teck Metals) from the reaction shaft. Three in-line electrodes deliver the required power (5–7 MW at Teck Metals) to complete the slag reduction and to maintain the desired slag temperature between 1,320°C

**Table 6 Main typical operating data of direct lead smelting technologies at various plants**

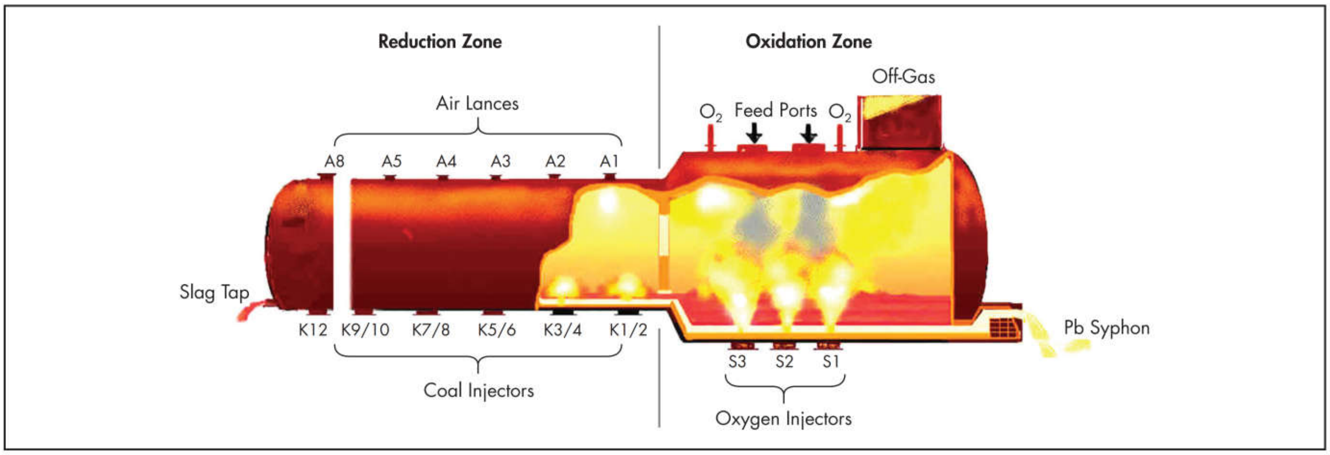
| Item | Kivcet (Portovesme, Sardinia) | Kivcet (Teck Metals, Canada) | QSL (Berzelius Stolberg, Germany) | QSL (Korea Zinc, South Korea) | TSL (Nordenham, Germany) | Kaldo (Boliden Metall, Sweden) |
|---|---|---|---|---|---|---|
| Lead production, t/yr | 100,000 | 85,000 | 105,600 | 130,000 | 125,000 | 35,000 |
| Raw material, t/yr | 150,000 | 325,000 | 176,000 | 314,000 | 190,400 | 43,000 |
| Primary/Secondary ratio | 3.5:1 | 1:2 | 1:1 | 2:1 | 1:2 | 1 |
| Types of secondaries | Battery paste, EAF-dust, zinc oxide, waelz oxide | Recycled battery, zinc plant iron residues, Pb plant drosses | Battery paste, zinc plant residues, slags, scrap | Pb-residues, Pb-Ag residues, battery paste | Battery paste, residues, scrap | |
| Dryer type | Rotary drum | Rotary drum | N/A* | N/A | N/A | Rotary drum |
| Feed rate, t/h | 35 | 58 | | | | 30 |
| Inlet moisture, % | 8–10 | 13 | | | | 5 |
| Outlet moisture, % | 0.1 | <1.0 | | | | <0.1 |
| Off-gas volume, Nm$^3$/h | 24,000 | 71,000 | | | | 15,000–20,000 |
| Feed rate, t/d | 600 | 1,220 | 612 | 1,500–1,600 | 670 | Batchwise |
| Moisture, % | <1 | <1 | 8–10 | 10–12 | 10–12 | <1 |
| Silica, kg/t bullion | 92.8 | 170 | 74 | 20 | 300–600 | |
| Lime, kg/t bullion | 154.4 | 480 | 230 | 117 | 500–1,300 | 203 |
| Iron, kg/t bullion | 23.2 | 540 | 150 | 148 | 500–1,000 | 217 |
| Coal, kg/t bullion | | 440 | 115 | 131 | | |
| Coke, kg/t bullion | 50 | 110 | 23 | | 1,000–3,000 | 48 |
| Oxygen volume, Nm$^3$/h | 6,500 | 9,100 | 3,570 | 9,400–9,900 | 1,600 | |
| Air volume, Nm$^3$/h | | 1,500 | 200 | 1,500 | 7,000 | |
| Oxygen enrichment in air | | | 67 | | 30–40 | Enrichment |
| Off-gas volume, Nm$^3$/h | 12,000 | 22,000 | 23,500 | 33,000–38,000 | 30,000 | 25,000 |
| $SO_2$–off-gas, % | 22–25 | ~15 | 14.1 | 10–15 | 6–7 | 4–5 |
| Steam, t/d | 300–350 | 670 | 300 | 480 | 340 | |
| Bullion, t/d | 300 | 260 | 370 | 440 | 139,000 | Batchwise |
| Matte, t/d | 10 | 13 | 16.5 | | 5,800 | |
| Slag in t/d | 120 | 590 | 274 | 300 | 46,000 | Batchwise |
| Pb in slag, % | 4 | 5.9 | 3–4 | 4–6 | 50 | 4.2 |
| FeO in slag, % | 26 | 27.9 | 29.2 | 27–29 | 11–12 | 40 |
| $SiO_2$ in slag, % | 22 | 21.6 | 20 | 20–22 | 5–7 | 21 |
| CaO in slag, % | 20 | 13.3 | 20.8 | 14–15 | 2–3 | 28 |
| Zn in slag, % | 9 | 18 | 8.8 | 15–16 | 6–10 | 4.6 |

Source: Adapted from Hayes et al. 2010
*N/A = Not available.

and 1,360°C. The majority of the zinc contained in the raw materials reports to the slag in the reaction shaft area. After entering the electric furnace compartment, the zinc is volatilized, depending on the adjusted reducing atmosphere, and recovered as fume. Slag is discharged from the Kivcet furnace at regular intervals and can be granulated or transferred to a subsequent slag-fuming furnace. The bullion is discharged at 850°–950°C through specially designed tapping inserts. Any matte generation in the furnace causes significant operational problems with bullion tapping. Its formation is minimized by controlling reaction shaft desulfurization and by tapping bullion at high temperatures to keep sulfides in solution. The bullion is transferred to a downstream refinery for further refining (Goosen et al. 2000).

Compared to the conventional two-step process, the off-gas volumes are much smaller (21,000 Nm$^3$/h at Teck Metals; 12,000 Nm$^3$/h at Portovesme) and contain $SO_2$ concentration of 12%–15%. This can be attributed to the application of nearly pure oxygen and the sealed design of the furnace. The off-gases enter a waste heat boiler system. The outlet gas temperature from the waste heat boiler is approximately 350°C. Typically the boiler system produces steam (23–25 t/h at Teck Metals; 12–15 t/h at Portovesme). In the Portovesme plant, the thermal energy is converted in a turbine into electricity, which is utilized in the process minimizing outside energy requirements. The collected dust in the waste heat boiler is, together with the dust precipitated in the subsequent hot-gas electrostatic precipitator, recirculated back to the process. The most recent available operating data of both Kivcet plants in operation are listed in Table 6 (Siegmund 2000a; Hayes et al. 2010).

**QSL/SKS technology.** The QSL (Queneau–Schuhmann–Lurgi) technology is a continuous-operating single-vessel bath smelting process. The process principles were developed and patented by two Americans, Professor Paul E. Queneau and Professor Reinhardt Schuhmann Jr. Based on a patent developed by the German companies Lurgi AG and Berzelius Metall GmbH, the QSL process for the recovery of lead advanced



Adapted from Pullenberg and Rohkohl 2000. Copyright 2000 by The Minerals, Metals & Materials Society. Used with permission.

**Figure 10 QSL converter at Berzelius Stolberg GmbH**

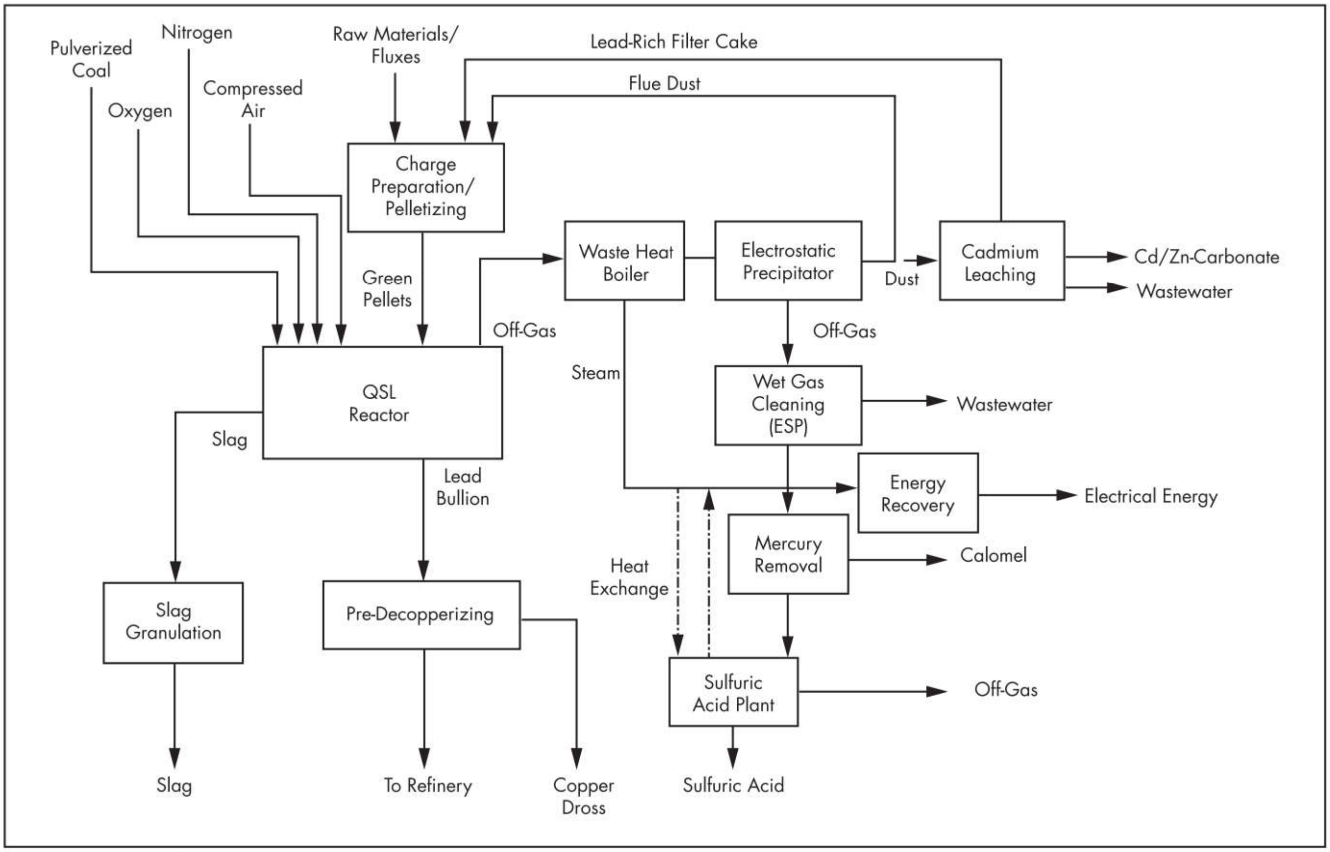
to an industrial scale after operating a semicommercial plant for several years (Queneau and Siegmund 1996). Today, three plants based on the QSL technology are in operation: two at Korea Zinc in Ulsan, South Korea, with annual lead production of 250,000 t, and one at Berzelius Stolberg GmbH in Stolberg, Germany, with annual lead production of ~150,000 t.

The entire converting process is incorporated in one slightly inclined (0.5%), closed, kiln-like smelting unit. The converter is divided by a partition zone into smelting and slag reduction zone (Figure 10). It can be tilted by 90 degrees about its longitudinal axis when the process is interrupted. The process is designed to treat all grades of lead concentrates as well as secondary materials, applying the bath smelting principle with submerged high-pressure injection of tonnage oxygen and fossil fuels (Siegmund et al. 1998). Two converter sizes are applied. The QSL-converter at Korea Zinc has a diameter of 4–4.5 m and an overall length of 41 m, while the converter at Berzelius has a diameter of 3–3.5 m and a length of 33 m. The current ratio of primary to secondary material at the smelter in Ulsan is 2:1 and in Stolberg almost 1:1. Both operations, however, report a high flexibility of the process in terms of feed composition. They can deal with a wide variety of feed materials and quickly adapt to changes in the feed composition. Rates of secondary materials of more than 60% have been charged (Siegmund 2000b).

The feed preparation is relatively simple, consisting only of bins for material storage, weighing devices for composing the anticipated charge mixture, and a mixer to thoroughly blend and agglomerate the charge to satisfy steady-state feed requirements. Lead scrap materials can be directly charged into the converter. The moist and agglomerated feed mixture is then charged homogeneously and weight controlled through feed ports located in the roof of the smelting compartment into the converter. It falls into a dispersed molten mixture consisting of primary slag and crude lead while oxygen is injected through submerged gas/water aerosol-cooled tuyeres at the bottom of the converter. In the liquid bath, an autogenous roast reaction smelting is initiated, converting some of the lead compounds directly into low-sulfur lead bullion and forming a primary slag with a lead oxide content of 40%–50%. The exothermic reaction takes place at 1,050°–1,100°C. As fuel, low-cost available materials like bituminous coal or petroleum coke can be applied. The slag flows through a submerged opening in the partition wall into the slag reduction zone where the lead oxide is gradually reduced to metallic lead using pulverized coal as the reducing agent while the slag flows to the opposite end of the converter. The coal is injected with a carrier medium into the melt through a series of bottom-blowing gas-cooled injectors together with a controlled amount of supplementary oxygen to adjust the desired reduction potential in the melt. The independently and accurately controlled gas analysis injectors are spaced sufficiently apart to form a series of proper reaction gas-slag bubble plumes of sequentially decreasing oxygen activity and increasing temperature until slag is discharged. These chemically active mixing areas are separated by passive lead settling zones. There is virtually no interaction of adjacent bubble plumes, thus creating a continuous mixer–settler configuration (six).

At the end of the slag reduction zone, a larger settling area is provided to accomplish sufficient separation between the low-lead slag and the lead. The settled metallic lead flows countercurrently to the slag back into the smelting zones. It combines with the primarily produced lead bullion before being tapped through a siphon system for subsequent conventional refining. The final slag is tapped at the end of the slag reduction zone and granulated. The carbothermic reaction is endothermic and takes place at 1150°–1,250°C. Desired post-combustion of the process gas in the atmosphere of the slag reduction zone is accomplished with oxygen-enriched air, which is injected via lances located in the roof of the converter. The gas temperature is adjusted to 100°–150°C above the slag temperature to transfer heat back into the slag and contributes to the required temperature increase in the slag (Siegmund 2000a).

The QSL process applies nearly pure oxygen, which contributes to a comparatively small volume of highly $SO_2$-rich off-gas. The actual off-gas volume for the plant in Stolberg is 23,500 $Nm^3/h$ with more than 18% $SO_2$, depending on the type of concentrates. For the Korea Zinc plant, the off-gas volume is approximately 35,000 $Nm^3/h$ with $SO_2$ concentration between 10% and 15%. In the Stolberg converter, the off-gas from the reduction zone is combined with the generated off-gas in the smelting zone through an opening for the passage of the process gas, whereas the converter at Korea Zinc has a completely closed partition wall separating the off-gases from both zones. Depending on the adjusted gas atmosphere in



Source: Queneau and Siegmund 1996

**Figure 11 Process block diagram of a QSL plant**

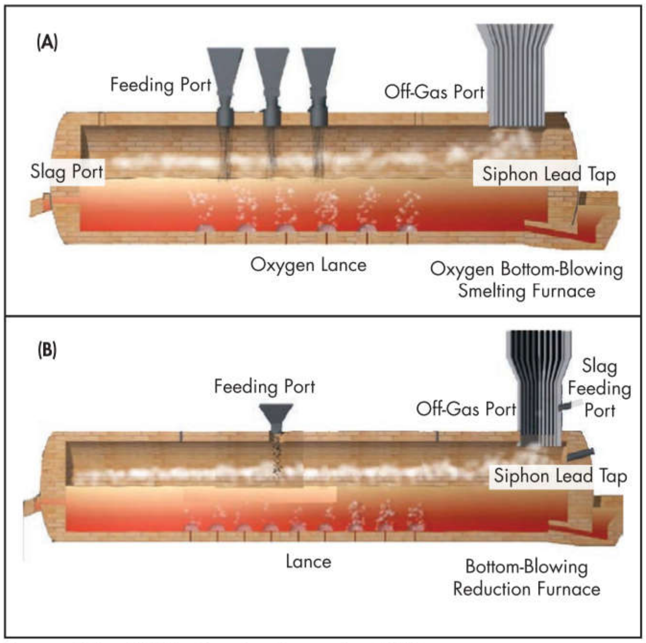
the slag reduction zone, the resulting process gas contains zinc fumes. The gas exits the converter through a second uptake and the fumes are collected for subsequent zinc recovery. This lowers the cost of the slag-fuming operation carried out in a separate furnace.

The produced slags contain 5% Pb on average in the Korea Zinc plant and 2%–4% Pb in Stolberg. It was demonstrated already that discharge slag of well less than 2% are obtainable, but only when zinc is simultaneously fumed at strong reduction potentials. In Stolberg, the zinc is then collected in the flue dust. This is undesirable because the flue dust is being directly recirculated to the converter and it would contribute to a substantial proportion of total feed by weight. Slags containing more than 15% Zn generally become too viscous at adjusted converter temperature. Heat is recovered from the off-gas in both plants and utilized to minimize outside energy requirements. In general, the off-gases are cooled in a waste heat boiler system consisting of a vertical radiation channel and a subsequent convective pass. In the vertical uptake, the gases are cooled to below 700°C. The exiting temperature of the off-gas after the convective pass is between 350°C and 380°C. Collected dust from the primary gas system is immediately recirculated back to the process. The $SO_2$-rich off-gas enters a double-catalysis sulfuric acid plant to produce sulfuric acid at conversion rates of 99.5% (Meurer and Ambroz 2010).

The general process block diagram of a QSL plant is shown in Figure 11 and the current main operating data of both QSL facilities are summarized in Table 6 (Püllenberg and Rohkohl 2000).

The concept, design, and operation of the SKS process is very similar to the QSL technology. It is a semicontinuous bath smelting process applying submerged cooled injector technology. It was developed in the 1990s mainly by Shuikoushan (SKS) Mining Bureau and Beijing Central Engineering and Research Institute for Non-Ferrous Metallurgical Industries. Opposite to the QSL process, the SKS technology consists of two independently operating refractory-lined cylindrical vessels, which are connected through a launder. Today, more than 20 lead smelters in China and one in India operate on the SKS technology concept. The current process went through three development stages. Initially the technology comprised only the smelting stage as a substitution of the sinter machine, followed by the slag reduction step in a blast furnace. The second generation of the technology employed the smelting reactor from where the generated slag was discontinuously discharged into a converter-type vessel with side-blowing tuyeres. The third and current generation consists of a combination of smelting reactor and a horizontally aligned slag reduction converter with bottom-blowing injectors, which are connected through a launder. By adopting the bottom-blowing electrothermal reductive furnace concept and utilizing the heat from the molten lead oxide slag, the reductant and fuel consumption efficiency is further improved compared to the second generation (Li and Yang 2010).

The feed preparation is identical to the QSL process and the charge (lead concentrates, secondaries, and additions) is



Source: China ENFI Engineering Corporation 2010

**Figure 12 (A) SKS and (B) RSKS furnaces**

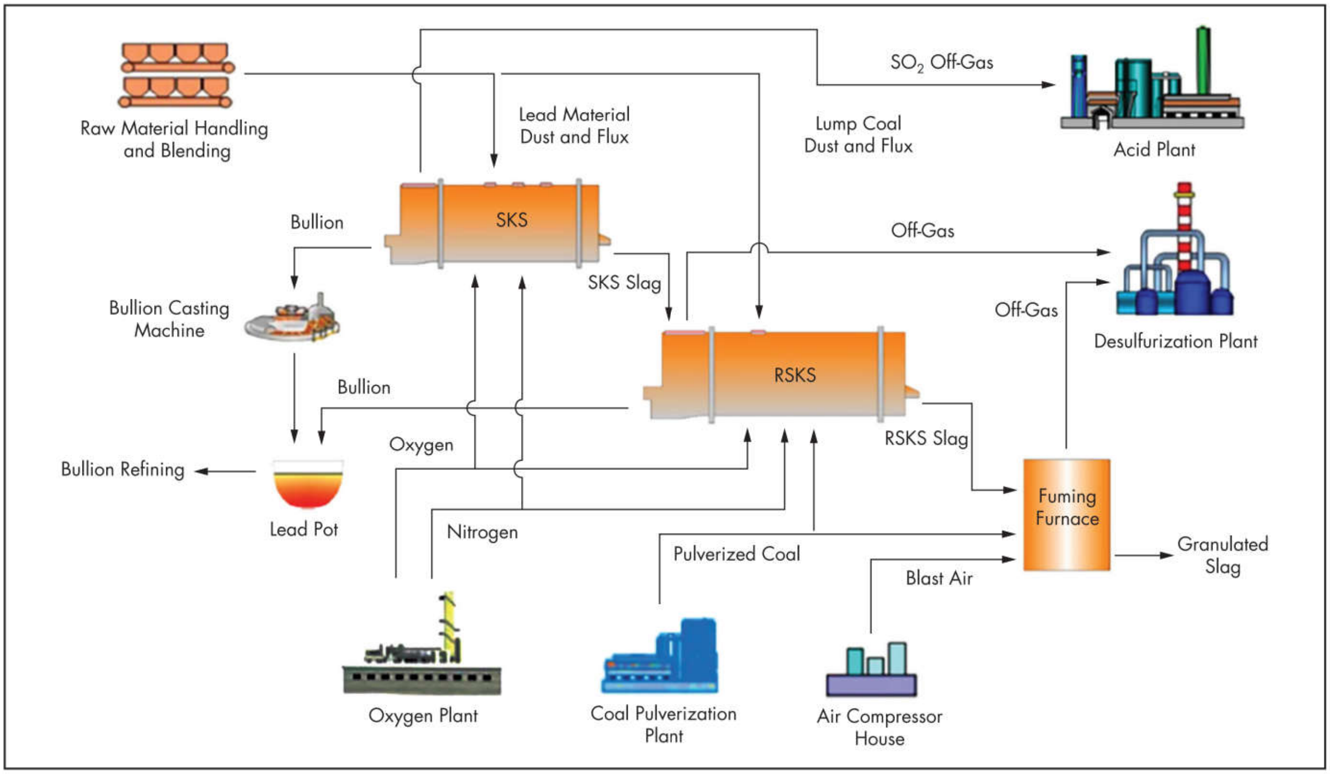
fed from the top. Oxygen, nitrogen, and atomized water are blown into the SKS furnace through bottom-blowing supersonic injectors accomplishing effective mixing and highly efficient smelting at excellent mass and heat transfer conditions (Figure 12A). The lead-bearing materials are rapidly oxidized and the exothermic reaction from the oxidation of sulfides provides sufficient heat to facilitate autogenous smelting. The majority of the lead is oxidized and reports to the lead-rich slag with some direct primary lead production. This amount depends on the composition of the charge and the adjusted oxygen potential in the bath. The production of a low-calcium slag allows furnace operation at relatively low temperatures, which are controlled at about 1,050°C. To ensure the appropriate properties of the slag, some limestone is added in the smelting stage. Volatile dusts from the oxidation stage containing lead, zinc, arsenic, cadmium, antimony, and other elements are collected in appropriate dust collection systems and recirculated to the smelting step. The dust generation depends upon the prevailing metal compound and its associated vapor pressure under oxidizing atmosphere and temperature. To minimize the generated dust amount, the oxygen potential is maintained at an appropriate level to minimize the presence of lead sulfide, which has a significantly higher vapor pressure at prevailing temperatures than that of lead bullion and lead oxide. Furthermore, the smelting temperature is kept as low as possible to minimize the vapor pressure of the various lead-bearing materials. The injection of pure oxygen into the furnace reduces the process gas volume, resulting in less mechanical entrapment and volatile dust formation (China ENFI Engineering Corporation 2010).

When the SKS furnace reaches a bath level of about 1.6 m, lead-rich slag will be tapped into an independently operating reduction SKS (RSKS) furnace through a hot-feed port (Figure 12B). Lump coal in small amounts is fed to the furnace through a cold-feed port. Oxygen and pulverized coal are injected into the furnace through bottom-blowing injectors. The bath temperature and the desired reducing atmosphere for the reduction process is controlled by predominately adjusting the feed rate of coal (lump and pulverized coal) and oxygen. When lead in the RSKS furnace slag is reduced to about 2% or less, the reduction process is stopped and slag is tapped. The furnace temperature fluctuates within a range of 1,200°C to 1,280°C, mainly based on the concentration of ZnO in the slag. The slag temperature was initially regulated through electrodes submerged into the bath from the top, ensuring a low slag viscosity and smooth tapping. The continuous or discontinuous use of electrodes in the RSKS furnace makes it more suitable to treat high-Zn materials with high melting points (Li and Yang 2010). Meanwhile, through further optimization, it was possible to eliminate the requirement of applied electrodes introduced from the top of the furnace, simplifying its operation.

Batch feeding and batch slag tapping in the RSKS furnace has advantages compared to continuous feeding and slag tapping. Lower lead contents in the final slag are easier to achieve at an increased lead recovery rate. Moreover, reduction takes place in an independent furnace with a single-gas atmosphere. The overall process flow diagram as shown in Figure 13 is very similar to the QSL flow sheet (Figure 11), with the exception of the slag fuming furnace addition.

**TSL technology.** The TSL technology is derived from the Sirosmelt top submerged lance process. That technology has been developed over the past 20 years in laboratory- and pilot-plant-scale studies on the recovery of almost the complete range of nonferrous, ferrous, and precious metal materials and is successfully applied in the copper, nickel, silver, tin, and zinc industries (Creedy et al. 2010). The initial design for lead smelting consisted of a two-furnace arrangement and is marketed today by the companies Outotec under the name Ausmelt and Glencore under the name IsaSmelt. Concepts for both technologies are very similar with only a few differences. For primary lead smelting, four IsaSmelt and six Ausmelt furnaces are commercially in operation. The first TSL lead plant was commissioned in 1996 at Recylex in Germany with the intention to perform the two-stage operation for lead recovery in a single furnace. The smelter has a design production rate of 90,000 t/yr of lead based on a certain ratio of primary to secondary raw materials (Karpel 1998). However, today, only the first smelting stage is conducted in the furnace. The high-lead-containing slag is processed elsewhere (Kerney 2010). Korea Zinc contracted with Ausmelt for the second lead smelter. It was commissioned in 2000 and processes lead oxide fume, sulfate residue, and battery paste. The process concept and the principles of the furnace design are illustrated in Figure 14 (Errington et al. 2010).

Raw materials and additives are stored in bins from where a feed delivery and weigh control system collects and composes the desired charge composition and transports it to a mixing device for blending and homogenizing before being fed into the furnace. As in the QSL/SKS technology, the materials do not have to be dried or reduced to a specified material size before charging, and the principal process flow sheet is similar. The coarse, moist, and agglomerated charge is dropped through a feed port located in the inclined roof hood of the furnace and incorporated into the melt. Required air, process fuel, and fine materials are injected beneath the surface of a liquid slag bath through a top-entry submerged lance system. Oxygen-enriched air to levels up to 50% may be used with the specially designed lance, injecting the gas



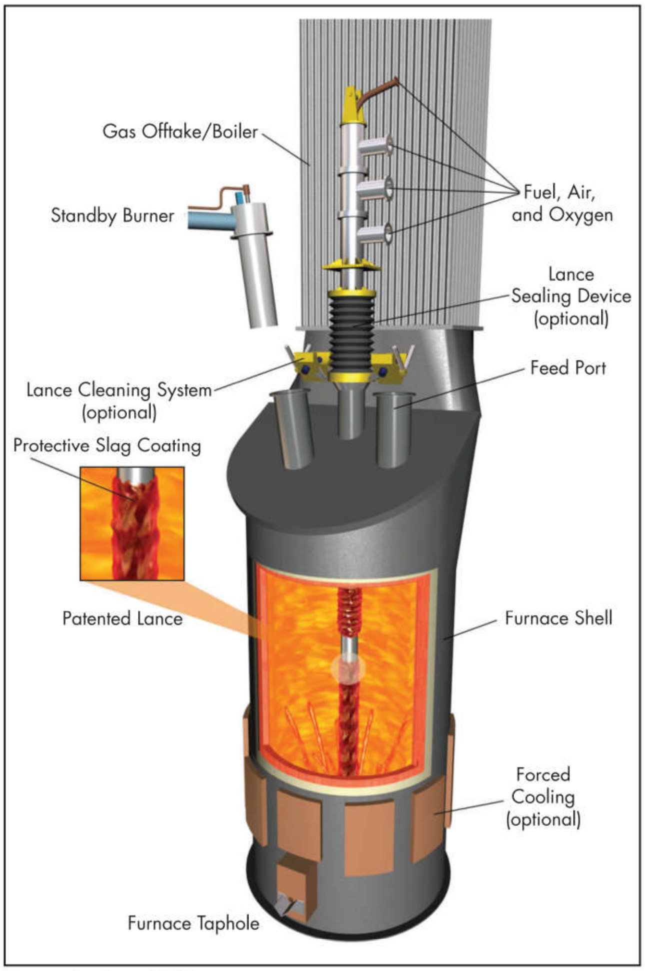
Source: China ENFI Engineering Corporation 2016

**Figure 13 Typical process flow sheet SKS-RSKS technology**

through the outer annulus while the fuel and the fine materials are conveyed down the lance through an inner tube. The stainless-steel lance is protected from the furnace contents by a coating of frozen slag to minimize lance wear. The coating is established by carefully lowering the lance into the furnace with an intermittent stop above the bath permitting slag to splash and freeze on the lance before submerging the tip of the lance. During operation, the latter is always below the theoretical static slag line. The media are therefore injected into the slag, creating very turbulent conditions in the furnace, promoting very rapid reactions, and resulting in high smelting capacities in small areas. The furnace is usually constructed as a refractory-lined cylinder applying a high-quality chrome-magnesite refractory lining. Where very aggressive slags, mattes, or metals are present or higher temperatures are employed, water cooling is applied behind the bricks to ensure acceptable refractory life.

A slag reduction process to produce bullion and discard slag follows the oxidation smelting process step. Precise control of the system oxidation state is a key feature of TSL technology. This, together with the addition of a reductant, such as coal, allows the reduction step to be precisely tailored to meet specific requirements. A low oxygen potential in the order of $10^{-9}$ to $10^{-10}$ atm is maintained. The liquidus temperature of lead-oxide-containing slags is raised from 1,000°C to 1,100°C to 1,150°C to 1,250°C as the lead in slag drops from more than 40% lead to about 10%. Fluxing with limestone may be needed to substitute lead oxide by calcium oxide and to prevent the precipitation of zinc ferrite or magnetite from zinc- and iron-rich slags with lead levels in the region of 15%–40% Pb in the temperature region of 1,200°C. Slag reduction is a less economic exercise than smelting of high-lead-content material directly to bullion, particularly with solid slag processed on a campaign basis. Lead oxide fume is produced in increasing quantities with increasing temperature, collected in a baghouse or electrostatic precipitator and recycled to the smelting furnace, with or without external fume treatment for impurity removal. In both stages, smelting and reduction, air is introduced into the top space of the furnace through a shroud pipe attachment on the TSL to post-combust any volatilized species. Up to 40% of the energy generated by these reactions is recovered for utilization in the bath (Kaye et al. 2008).

The overall process concept can consist of either single, batch, two-furnace continuous, two-furnace continuous and batch, or three-furnace continuous process options. The preferred approach for lead smelting is the two-stage approach where slag flows continuously from the smelting to the reduction furnace via weirs, siphons, and launders. A process block diagram of this alternative is shown in Figure 15. In general, the second furnace is smaller than the primary furnace, particularly when smelting high-grade feed. Even though the second furnace is smaller, it requires a separate gas handling system, typically incorporating an evaporative gas cooler and baghouse, and this increases plant capital cost above that of the single-furnace, two-stage operation. The final slag product from the second furnace typically contains low levels of lead but may well contain appreciable levels of zinc (8%–12% Zn). The slag can be granulated and held for long-term storage or a second slag reduction can be carried out to recover the zinc as a high-grade (>50% Zn) fume, as previously described, and produce a discard slag containing low levels of lead (<1% Pb)



Source: Stephens 2010

**Figure 14 TSL furnace design including schematic section**

and zinc (<3% Zn). The main operating data of the TSL operation in Nordenham, Germany, are summarized in Table 6.

**Kaldo technology.** Boliden Metall AB developed the Kaldo process, and its operation in Rönnskär, Sweden, is the sole application in the lead industry. The plant is used not only for lead smelting but also for the treatment of secondary raw materials containing copper, precious metals, and plastics. The process is based on the flash smelting principle and operates on a discontinuous/batchwise basis and consists of a top-blowing rotary converter. It has special features compared to the other processes. The batchwise operating mode seems to make the process not very suitable for large-scale operation, but the furnace is a very flexible unit and can treat a wide range of secondary materials, including battery scrap, residues, and recycled dust among lead concentrates. It was exclusively using concentrates from its own Laisvall mine as lead-bearing raw material but recently has been treating other concentrates. As in other flash smelting applications, the feed material has to be dried to moisture contents less than 1% before being blown through a lance into the furnace, where it reacts in the flash with the oxygen-enriched air that is introduced. Iron and lime fluxes are also added to bind the silica in the concentrate, generating a liquid slag. The generated slag contains high concentrations of lead oxide, which is reduced to average lead contents of ~4% by coke. The lead bullion and the slag are then discharged into separate ladles. The lead is subsequently treated in a refinery, while the slag is returned to a mine for final underground disposal. The converter is completely encapsulated in a vented enclosure, generating off-gas volumes of 25,000 $Nm^3/h$ with $SO_2$ concentration between 4% and 5%. The off-gases are combined with process gas from the adjacent copper smelter to produce sulfuric acid (Siegmund 2000a). Figure 16 illustrates the process flow sheet of the Kaldo process, and the main operating data are summarized in Table 6.

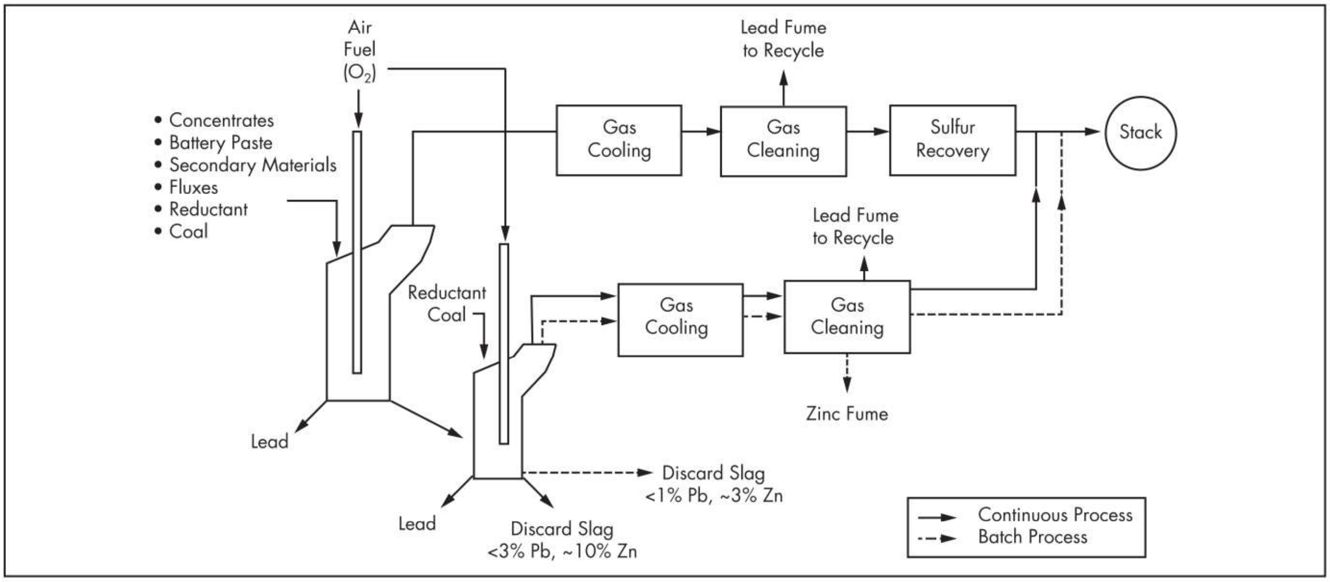


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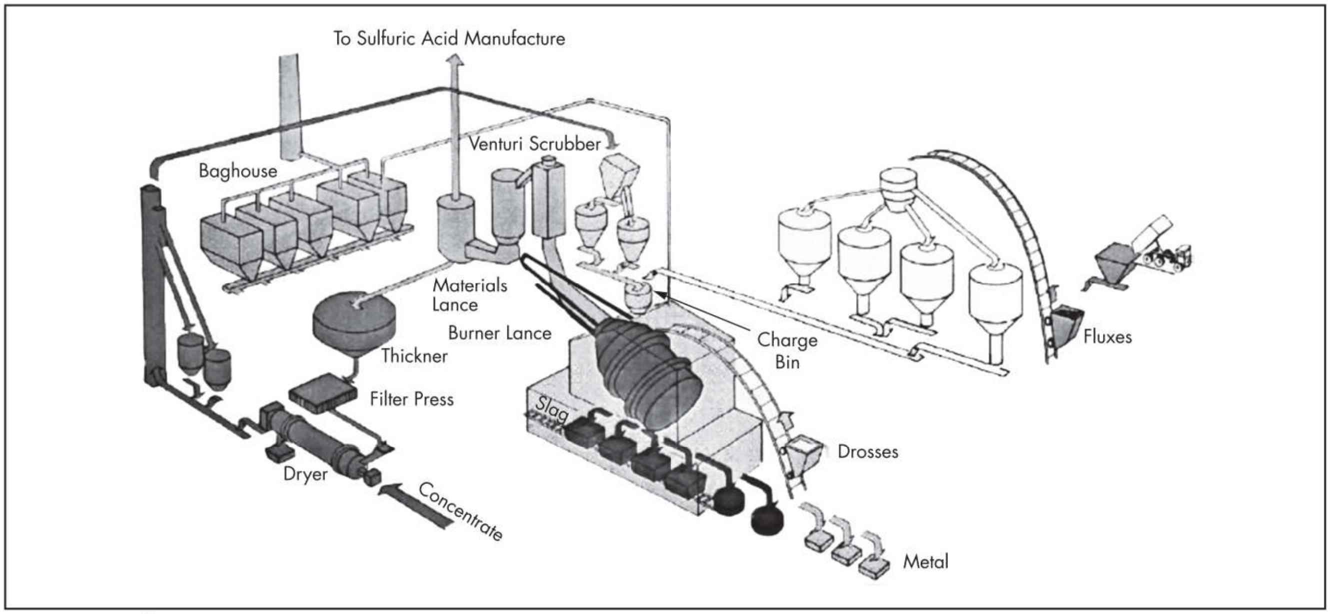
**Figure 15 TSL two-furnace process without zinc recovery**



Source: Siegmund 2000a

Figure 16 Isometric process flow sheet of the Kaldo technology

### *Secondary Lead Smelting*

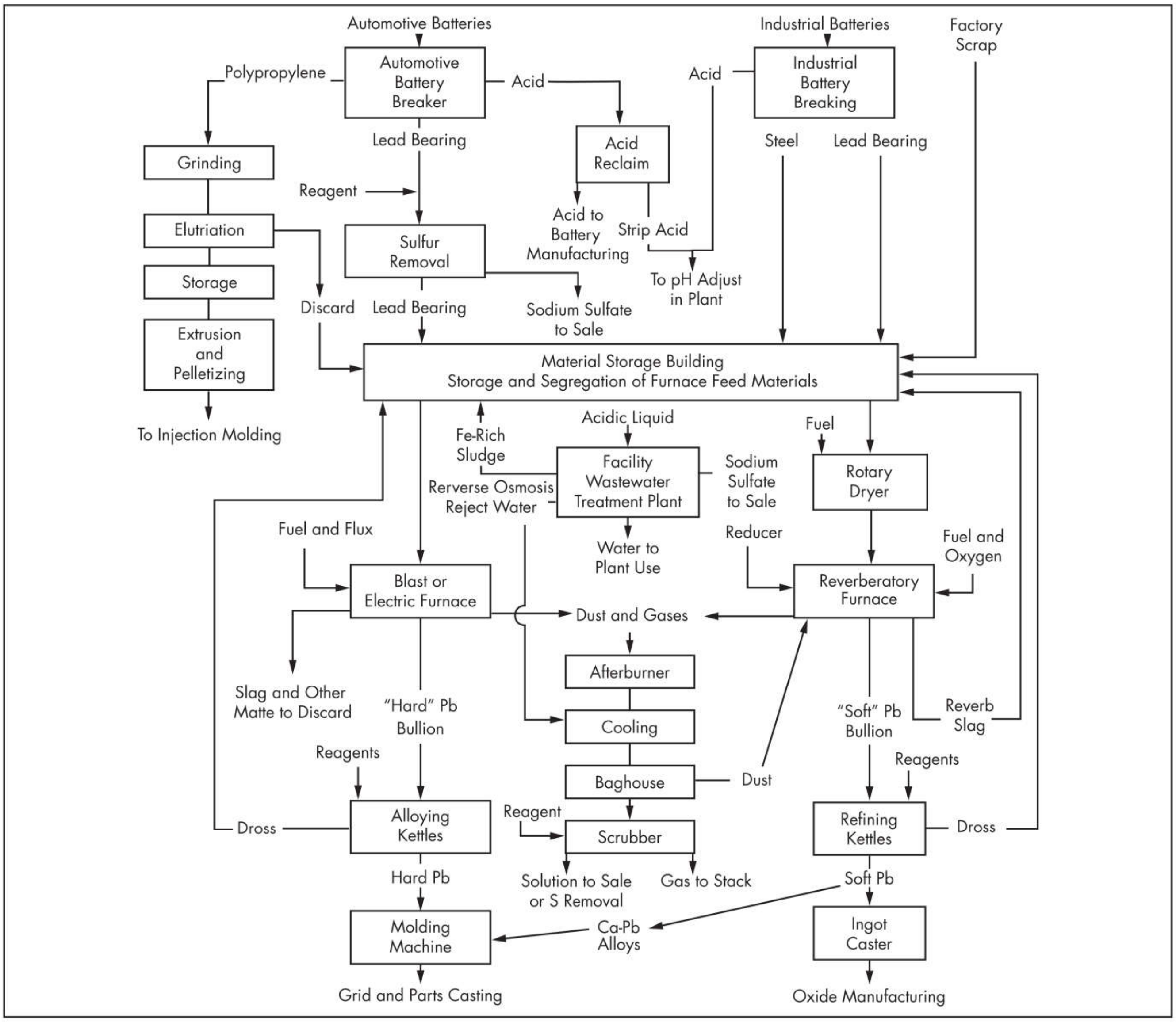
Process configurations for secondary smelters vary greatly from plant to plant, region to region, country to country, and continent to continent. There are always site-specific constraints, which affect the decisions of equipment, process, and design configurations. In Europe, the configuration of a secondary lead smelter is typically a battery-breaking plant in conjunction with a discontinuously operating short rotary furnace technology and a refinery. A few smelters apply blast furnace operation treating the entire, unbroken battery, while one smelter uses a lance-type furnace. Several lance-type furnaces have also been placed into operation in Australia and the Pacific Rim. The smelters in the United States employ reverberatory furnaces coupled with either blast furnaces or electric furnaces on a continuous basis (Siegmund 2001).

In the past, secondary lead smelters were almost exclusively producing lead and lead alloys, and controlling their emissions of flue dust, lead, and $SO_2$. By-products were either sold or discarded. During the last two decades, lead recycling experienced many technological innovations, mainly by the addition of physical separation and/or hydrometallurgical processing steps, resulting in a remarkable improvement in the utilization of the components contained in batteries. Additional advancements were motivated by the introduction of more stringent environmental legislation and health and safety regulations, the lead industry's recognition of its environmental responsibility, as well as economic considerations. Today, one of the objectives is not to eliminate or significantly reduce the generation of waste materials and by-products but to convert them into value-added products and return them to the battery manufacturer. Necessary modifications and expansions to the plant process flow sheet have been made at smelters. Waste sulfur is recovered in a crystallizer as sodium sulfate crystals, or ammonia solutions are generated for sale. Polypropylene is washed and cleaned for extrusion purposes and subsequent utilization of the granules in battery manufacturers' injection molding operations for battery cases and tops. Further process additions are, for example, the affiliation of an incineration plant to a German secondary lead smelter incinerating the nonrecyclable components of the scrap batteries obtained from the secondary smelter together with other combustible waste materials subject to recovering energy. Another German smelter produces high-quality polypropylene compounds with specific physical and mechanical properties, which is carried out by the accurate dosing of organic as well as inorganic additives. In the United States, one smelter purifies the sulfuric acid by-product from battery breaking for reuse in new batteries by employing a solvent extraction process (Siegmund 2010). The only real waste product is still the slag from the final reduction furnace, which is generated in a nonhazardous form. The current process flow sheet of a modern U.S. operation resembles Figure 17 (Leiby 1999).

**Battery breaking and component separation.** Typically, the primary material processed in a secondary lead smelter is the spent automotive lead–acid battery, which accounts for ~80%–90% of the materials received from off-site. This percentage may change depending on supply. Exact specifications for components of an auto battery vary from manufacturer to manufacturer. A typical auto lead–acid battery may have the average compositions shown in Table 7 (Siegmund 2001).

Until the early 1970s, batteries were broken manually, which involved sawing off the battery tops and dumping the contents into the furnaces for processing purposes. Casing components were either processed in a separation system to recover polyethylene/propylene or discarded. During the 1980s, the industry started to replace the existing system by installing automated facilities, which consisted of breaking the batteries and subsequently physically separating each spent automobile battery into its components by efficient gravity units (Queneneau et al. 1993).

Batteries are shipped to the plant in an environmentally safe manner in dump trucks or on pallets where they are unloaded and, if necessary, stored in an acid-proof warehouse. If acid recovery is desired, then the batteries must first



Source: Leiby 1999

**Figure 17 Typical process flow sheet for a secondary lead smelter in the United States**

**Table 7 Typical vehicle lead–acid starter (starting, lighting, ignition) battery**

| Components | Compound | Percentage | Total, % |
|---|---|---|---|
| Metallic lead (grids and poles) | | | 25 |
| Lead paste | $PbSO_4$ | 50–60 | 38 |
| | $PbO_2$ | 15–35 | |
| | PbO | 5–10 | |
| | Metallic lead | 2–5 | |
| | Other | 2–4 | |
| Polypropylene cases | | | 5 |
| Separators, hard rubbers, etc. | | | 10 |
| Sulfuric acid (~15%) | | | 22 |

Source: Siegmund 2001

be perforated or pre-crushed to allow the acid to be drained and collected. The batteries are reclaimed and loaded into a battery breaker, either a crusher with a tooth-studded drum or a swinging-type hammer mill. In the breaker, the batteries are shredded into small pieces for subsequent ergonomic separation into its components. Water is added to the breaker to slurry the paste. Efficient separation and concentration of the sulfur-rich paste is accomplished by screening in a rotating drum or on a vibrating screen, applying high-pressure water spray nozzles. The paste suspension is then pumped into tanks for chemically removing the sulfur or straight to a filtering device (press or belt) to recover paste. The remaining battery components are separated employing gravity-based hydroflotation separators. In these separators, the metallic lead sinks countercurrently to a water flow into a screw conveyor for removal from the system. The casing materials are carried away with the water and pass into a sink–float tank where polypropylene is separated by gravity from polyethylene, ebonite, and other plastic materials (PVC, glass fabrics, etc.). The entire process results in four intermediate products: (1) lead paste for smelting, (2) metallic lead for melting or smelting, (3) polypropylene for recycling purposes, and (4) lead-contaminated plastic fraction, which is disposed or, if permitted, can be charged to a furnace. Figure 18 illustrates a typical flow sheet of a battery-breaking plant applying the described process steps (Behrendt 2000).

Several smelters have installed a leach circuit to chemically remove sulfur from the paste prior to the smelting process to overcome three disadvantageous objectives during smelting: (1) reduction of $SO_2$ emission, (2) reduction of matte generation, and (3) minimization of the amount of slag. The sulfur removal can be achieved by using various reagents. The most common reagents are either caustic or soda ash producing lead hydroxide and sodium sulfate (Equation 26) or lead carbonate and sodium sulfate (Equation 27), respectively:

$$\mathrm{PbSO_4(paste) + 2NaOH(aq) = PbO(paste) + Na_2SO_4(aq) + H_2O} \qquad \textbf{(EQ 26)}$$

$$\mathrm{PbSO_4(paste) + Na_2CO_3(aq) = PbCO_3(paste) + Na_2SO_4(aq)} \qquad \textbf{(EQ 27)}$$

Both reactions decrease the paste's sulfur content from about 6%–7% to <1%. The process can be designed on a continuous or discontinuous basis. In both cases, the pH is closely monitored for accurate addition of reagent because of detrimental effects of the furnace operation. The reacted slurry is then sent to filter presses and the sodium sulfate solution to a crystallizer. Some facilities combine the liquid from their post-baghouse scrubber with the liquid from the reaction. The scrubber solution, however, requires oxidation to ensure that all the sulfites have been converted to sulfate prior to entering the crystallization process. The sodium sulfate solution is cleaned, crystallized, and dehydrated for sale.

In an alternative procedure, the battery pieces are conveyed from the breaker to a density gradient sink–float vessel with a media specific gravity of 1.4 g/cm$^3$. Plastic, hard rubber, and separators float and are conveyed to the plastic recovery system. Paste and grid material are moved by drag-chain conveyor and discharged onto a wedged-wire shake screen. Metallic material discharges into a screw conveyor and is transported to the raw material storage building. The paste slurry collected from the shake screen flows to a reactor tank for desulfurization, as described previously, or straight to a filtering unit. The desulfurized paste is filtered through a dewatering press with the effluent pumped to the on-site wastewater treatment plant. Desulfurized paste is discharged into the raw material storage building. The plastic recovery system consists of a hammer mill, primary and secondary sink–float washers, and pneumatic transfer to trucks for shipment. By-products (hard rubber and separators) are conveyed to the raw material storage building.

**Smelting of battery scrap material.** Ten years ago, materials for smelting were stored outside uncovered. Today, they are stored in an environmentally state-of-the art containment building. The materials may include slag, paste, and metallics from battery breaking, factory scrap, and some other raw materials that can be fed directly to the furnace, together with the lead-bearing material coming out of the battery breaker. Many buildings are equipped with a leak detection system and conform to all state and federal regulations. Coke products that are used as reducing agents and fluxes are also stored inside the containment building.

In the United States, the predominantly applied smelting technology consists of a multistep process consisting of selective reduction smelting of the raw materials in a reverberatory furnace coupled with slag reduction in either a blast furnace or electric furnace. This combination allows producing low-antimony "soft" lead bullion from the reverberatory furnace. The slag reduction unit treats the PbO-rich "reverb" slag as well as recycled dross from the refinery to concentrate the alloying elements (mainly antimony, tin, and arsenic) in the "hard" lead bullion (Stout 1993). This is used to generate various alloys required for different structural parts in the batteries. The raw materials are typically mixed and passed through a drying system before being charged to the reverb. A typical charge consists of 85% battery breaker material, 5% mud from the desulfurization process and wastewater plant, 5% refinery dross, and 5%–10% internal scrap. In addition to these materials, all the plastic recovery system by-products are fed in the mixture working as reducing agents and possessing some calorific value inside the furnace. One major secondary producer in the United States uses an electric furnace rather than a blast furnace, at two locations. This allows them to directly connect both furnaces, providing an overall continuous operation. Higher slag temperature in the electric furnace also permits the production of an environmentally more-stable slag and results in lower flux consumption, decreasing slag volume by about one-third. Recovery of lead, antimony, and particularly tin is increased. The discard slag from both reduction furnaces is characterized by an iron–lime matrix and has to pass an elution test to demonstrate leachability of the RCRA metals below the permitted toxicity levels defined in the Resource Conservation and Recovery Act of 1976. Typically, the slag is ground and combined with stabilization agents like cement or phosphates prior to going to the landfill.

In Europe, lead bullion is most commonly produced in short rotary furnaces. They provide a high flexibility in handling feed materials but are batch-type furnaces. The metallic lead grids, desulfurized or non-desulfurized lead paste, scrap metal, and lead-rich residues (flue dust, slimes, dross) can be either together, separate, or in each combination smelted at temperatures of about 1,000°C. Depending on the selected charge composition, "soft" or "hard" lead bullion can be produced. In the past almost exclusively, a soda-based slag was generated to capture the remaining sulfur, minimizing emissions. To produce environmentally more stable slags, many secondary lead smelters have changed the slag composition to a soda-containing slag with a silica matrix, or entirely to a fayalitic slag. Discard slag is disposed in a landfill. Recent investigations are focusing on stabilizing the slag so that it can be used as construction material in combination with other materials, avoiding high disposal costs. Alternatively, long rotary furnaces can also be applied treating secondary feed material. One long rotary furnace, for example, operates in Canada. Some plants in Europe and Asia smelt the secondary lead material in a blast furnace without breaking the batteries in a breaker system. The batteries may be pre-crushed with a front-end loader before being charged to the furnace, mainly to drain the sulfuric electrolyte contained in the battery. Only

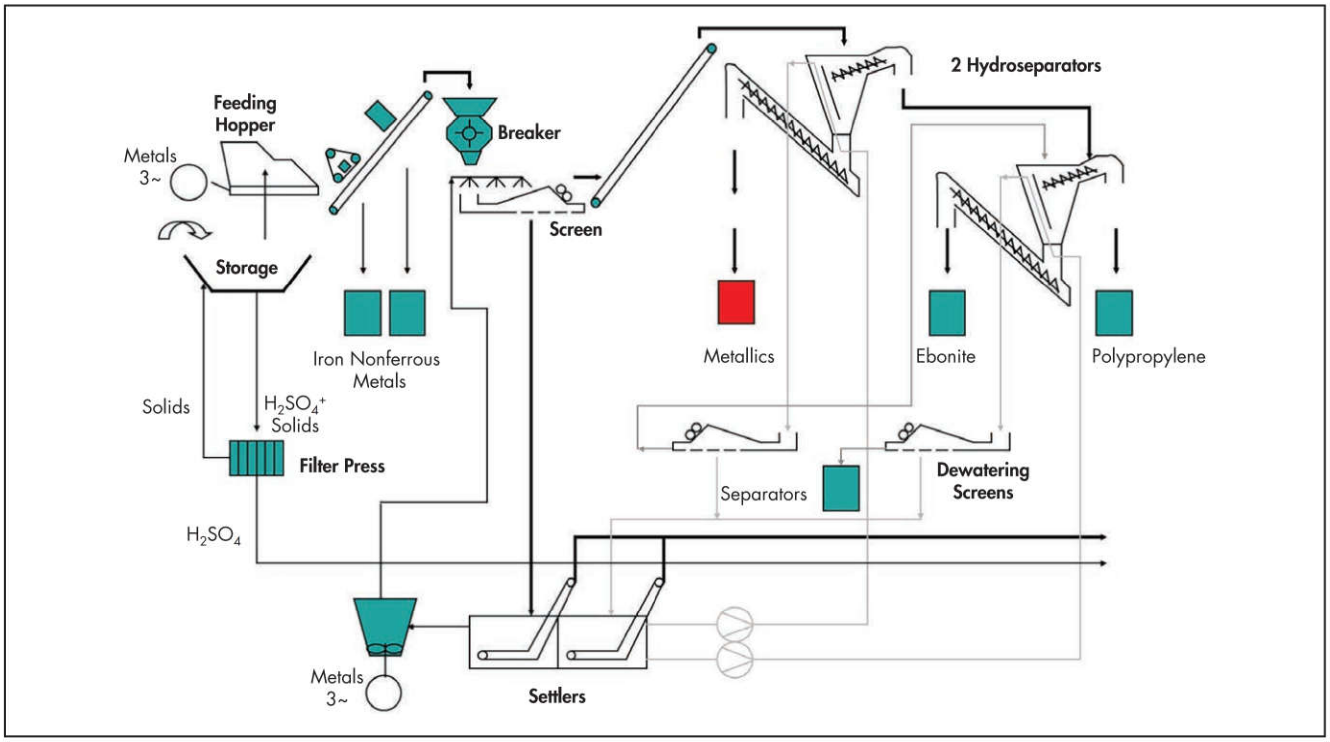


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**Figure 18 Process flow sheet for a battery-breaking plant**

one type of bullion is produced, and the generated slag is primarily iron-silica-lime containing slag. Sulfur is captured as a matte. A one- or two-step TSL furnace system is also employed as a suitable smelting concept for battery scrap after battery breaking (Siegmund 2001).

Since all secondary smelters are required to control their sulfur dioxide emissions, sulfur is either removed prior to smelting in a desulfurization step of the paste or by scrubbing sulfur dioxide from the off-gas or tying it up as a matte. Some smelters are scrubbing with caustic and lime, combining the resulting solution with dilute acid from the raw material storage, making gypsum. Others are scrubbing with caustic and oxidizing the solution prior to making sodium sulfate crystals or handling it in the wastewater treatment facility. At one smelter, sulfur dioxide is scrubbed with ammonia. After several purification steps, the resulting anhydrous ammonia is sold as a raw material to the fertilizer industry. All smelters are well equipped with efficient fabric filter systems to minimize and control the dust and heavy metal emissions. In addition, many smelters have meanwhile implemented a complete enclosure of the buildings, which further minimizes emissions. Efficient filter systems, integrated dust cleaning and flue gas cleaning systems continuously remove both dust and lead to comply with the local environmental regulations on a permanent basis.

**Recovery of polypropylene.** As battery manufacturers became more vertically integrated, polypropylene became a valuable by-product for the smelters. They implemented compounding plants producing recycled polypropylene granules for their battery customers. The raw material for the production of polypropylene compounds is the shredded polypropylene fraction from the separation of the casings of lead–acid battery scrap in the battery-breaking area. Before being transferred to the compounding plant, the collected polypropylene chips actually undergo intensive preparation steps. In a milling unit, they are washed to remove any remaining paste and dust, shredded to a smaller and more homogeneous fraction in a knife mill, and dried to evaporate all remaining moisture. Based on the prevailing quality of the polypropylene fraction from the milling unit, it can be either processed in a single or twin extruder to a product suitable for injection molding of new battery cases or upgraded to a highly valuable product by the application of specific refining procedures. One smelter in Germany concluded, after a detailed economic and ecological analysis, that the high valuable product route was the more suitable application of the two technically viable choices for its purposes. Main equipment of the plant is a twin-screw extruder, a filter system, a granulator, and a dryer. The clean polypropylene pieces and the additives are fed continuously to the twin-screw extruder. The extruder is designed in particular for the requirements of the polypropylene material and consists of several individual heated chambers to maintain desired extruding conditions. The charge mixture is melted under carefully controlled operating parameters and subsequently mixed with additional components according to predetermined specifications to obtain a homogeneous melt.

Today, the continued improvement of the refining process of recycled polymers results in an economic and environmentally compliant solution producing high-quality polypropylene compounds, which can be applied in many diversified industrial areas. The most dominant product group, however, consists of components for the car industry (85%). Popular applications in that area are fender liner, headlight and air suction filter casings, V-belt covers, cable covers, and so forth. But Seculene PP (polypropylene) materials are also used in the electronics industry as components for washing machines, dryers, vacuum cleaners, and dishwashers (Martin and Siegmund 2000).

### *Alternative Technologies for Secondary Lead Smelting*

During the last two decades, substantial research and pilot-scale testing has been carried out, and some technologies are still under development.

**Electrowinning.** At least three leach–electrowin processes have been tested on a pilot-plant scale in the past. All three processes have a different approach, but none of these technologies have yet been applied in a commercial operation (Leiby et al. 2000; Olper et al. 2000). This can be attributed to constant technological and ecological improvements in the existing smelting processes as well as for economic reasons. Today, Engitec Technologies is the only company actively pursuing to establish a commercial-sized operation of an adapted version of the electrowinning process in combination with elemental sulfur recovery in a bioprocess. After breaking the battery scrap in a conventional breaker, the paste is treated in a biosulfidization, which converts all lead-containing salts and/or oxides in the paste into PbS by means of anaerobic bacteria. The precipitated PbS and metallic lead content in the paste is then leached with the ferric fluoborate solution. Lead is dissolved and an elemental sulfur-based residue is generated. The grids-and-poles fraction is leached separately but also with ferric fluoborate solution. This promotes the distinguished production of refined lead and antimony–lead alloys. Subsequently, lead is recovered from both solutions by electrolysis in a FLUBOR diaphragm divided cell to produce lead cathodes in the cathodic compartment and to oxidize the ferrous ion to ferric ion in the anodic compartment, regenerating the leaching solution. As described in the literature, the process seems to have certain advantages but will require controls for the extremely aggressive acid that is employed. This technology was tested in the research lab of the Doe Run Company, treating primary lead sulfide concentrate with very promising results but has not been commercially implemented for economic reasons (Maccagni and Nielsen 2010).

**Plasma technology.** Several companies have developed technologies involving plasma arc furnaces that operate at very high temperatures. These have the potential to treat scrap material with low levels of contaminants, producing a discard nonhazardous slag. There have been two test furnaces built and operated, but the economics have not yet been successful.

## Pyrometallurgical Lead Refining

Smelting processes produce lead bullion that must be further refined to remove a range of impurities derived from ores, fluxes, and reagents. The maximum amount of impurities are up to 4,000 g/t Ag, up to 12 g/t Au, 1.5% Cu, 3.0% Sb, 0.5% As, 0.3% Sn, 0.3% Zn, 0.35% Fe, 0.003% Ni, 0.1% Bi, and 0.15% S. There are two principal lead-refining techniques practiced. Either a pyrometallurgical or electrolytic refining method is employed, mainly depending on the quality of refined metal required, the necessity to remove bismuth, the relative power cost, and the efficiency and cost of by-product recovery.

The most commonly used method is the pyrometallurgical refining process, which consists of multiple steps incorporating decopperization; softening by air/oxygen blowing or alternatively using a treatment with sodium salts (Harris process) to remove antimony, arsenic, tin, and tellurium; Parkes process removal of silver and gold with subsequent dezincing; and final caustic treatment of bullion. Where bismuth is found in the charge, the Kroll–Betterton debismuthizing process, or some variant of it, will be included as the penultimate step in the molten lead refining process. The various removal operations are conducted in a certain sequence and batch methods are usually applied to avoid re- or cross contamination of previous or subsequent drosses (Richards et al. 2010). The sequence of treatments, or the number of these steps, is governed by the impurity content of the bullion. However, the developments and implementation of continuous processes for each refining step have resulted in the successful implementation of semicontinuous refining operations in a few smelters. In secondary smelters, the applied refining method is very similar, with the exception of not employing the Parkes process for precious metal removal. By-product metals recovered in salable form are copper as matte or matte speiss, antimony as antimonial lead, and silver and gold by treatment of the Parkes process zinc crusts. A typical sequence of stages of pyrometallurgical lead refining in primary and secondary lead smelters is shown in Figure 19.

Electrolytic refining by the Betts process is a preferred method for lead bullion where bismuth is present in large quantities. In this process, lead bullion anodes are electrolyzed in a lead fluosilicate-hydrofluosilicic acid electrolyte. Impurities in the lead remain as anode slimes and include bismuth, antimony, arsenic, silver, and gold. The slimes are processed for recovery of bismuth and precious metals and of antimony as antimonial lead. The drossing treatment of the bullion before electrolysis ensures the proper balance of antimony and arsenic for adherent slimes to be obtained. Usually the Sb + As content in anode lead is 1.25%–1.75% (Gonzalez 2010).

### *Copper Drossing*

Independently of the applied process route, the lead bullion is passed through a drossing stage prior to being further refined. This first stage of refining entails the cooling of lead bullion from the furnace(s) to about 450°–500°C to lower the

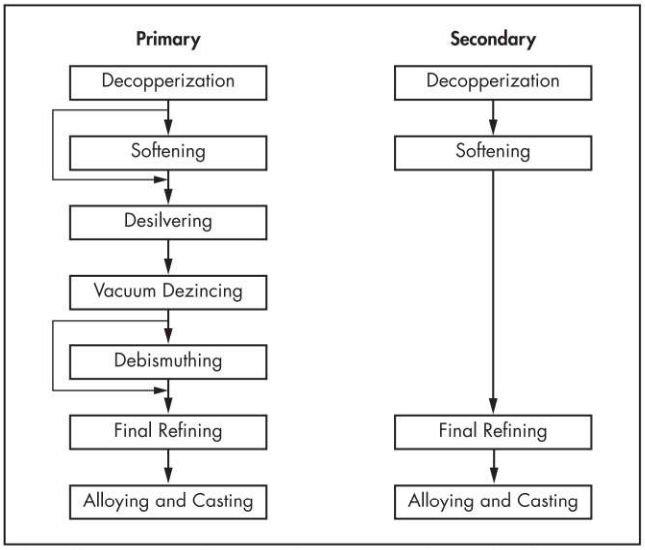

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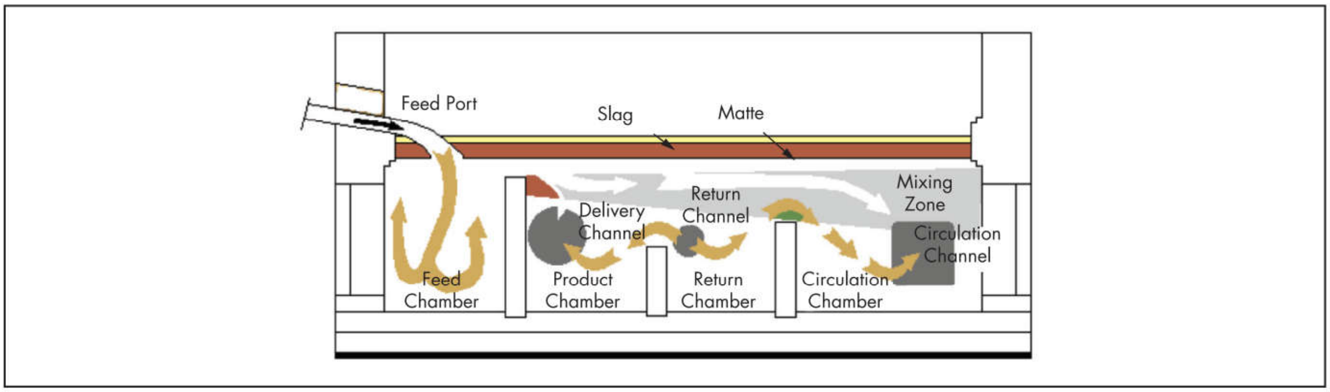
**Figure 19 Main process steps in pyrometallurgical lead refining at primary and secondary smelters**



Adapted from Richards 2010

**Figure 20 Continuous drossing furnace internals**

solubility of elements such as copper, iron, nickel, and zinc and precipitating them out as dross. Iron and zinc are usually almost completely rejected as oxides in the form of magnetite or spinels. According to the prevailing concentration of sulfur, arsenic, antimony, and tin in the bullion, copper precipitates as sulfide, arsenide, antimonide, or stannide. Nickel, if present, tends to follow the copper. Lead sulfide also forms at lower temperatures and enters into the dross. As copper dross begins to separate at about 750°C, the kettle will already contain a certain amount of dross at a working temperature of 450°–500°C. The formation of a solid dross cover is avoided by adequate movement of the bullion. The bath agitation also promotes the separation of entangled lead and "drying" of the dross. Carbonaceous materials such as coke, bitumen, or sawdust may be added to assist in the separation process of the entangled lead and to obtain dry dross. The drosses are transported to another building and processed further to copper matte and speiss.

### *Lead Decopperizing*

Lead bullion after drossing will contain equal or less than 0.5% Cu depending on the prevailing impurity concentration. An additional decopperizing step is required to reduce the copper content in lead bullion to levels of about 50 ppm, as required subsequently in the silver removal step.

Sulfur or pyrite/sulfur decopperizing is almost universally used for this purpose because of the strong affinity of copper to sulfur. The copper removal is accomplished by adding either lump elemental sulfur or a 4:1 pyrite sulfur mixture to the bullion at 400°–450°C in the vortex generated by a stirrer. Dross containing $Cu_2S$ and mostly PbS crystals with entangled lead is formed. Care must be taken not to move the molten bath too long after the sulfur addition is completed or to raise the temperature. Otherwise, copper will revert back to the lead according to

$$(Cu_2S)\text{dross} + Pb \rightarrow (2Cu)\text{bullion} + (PbS)\text{dross} \quad \textbf{(EQ 28)}$$

The kettle is then mechanically skimmed by an automated dross removal unit. The collected dross is being returned to the raw material storage for treatment in the smelter.

The two-step copper removal process is usually carried out batchwise, whereby the bullion from the furnace(s) is poured in a kettle and allowed to cool for drossing. For mechanical reasons (avoiding thermal stresses and premature failure of the kettles), a sump of drossed and cool lead always remains in the kettle. In both batchwise copper removal steps, a stirrer is applied to generate the required bath movement. After the formation of dry dross, the stirrer is replaced by an automated drossing machine, which removes the dross from the lead surface. Alternatively, a continuous decopperizing process has been developed in Australia and is applied in some smelters. The technology employs a reverberatory type furnace and combines both operating steps, drossing and decopperizing of the bullion. It is heated through roof burners and cooled in the hearth to generate the required temperature gradient for copper removal. The furnace illustrated in Figure 20 is divided into three compartments by partition walls and consists of three main areas: a compartment for the inflow of the bullion, a compartment for discharging matte and slag, and a circulation launder for cooling the lead and sustaining a bullion temperature at the bottom of the furnace slightly above the melting point of lead.

### *Softening*

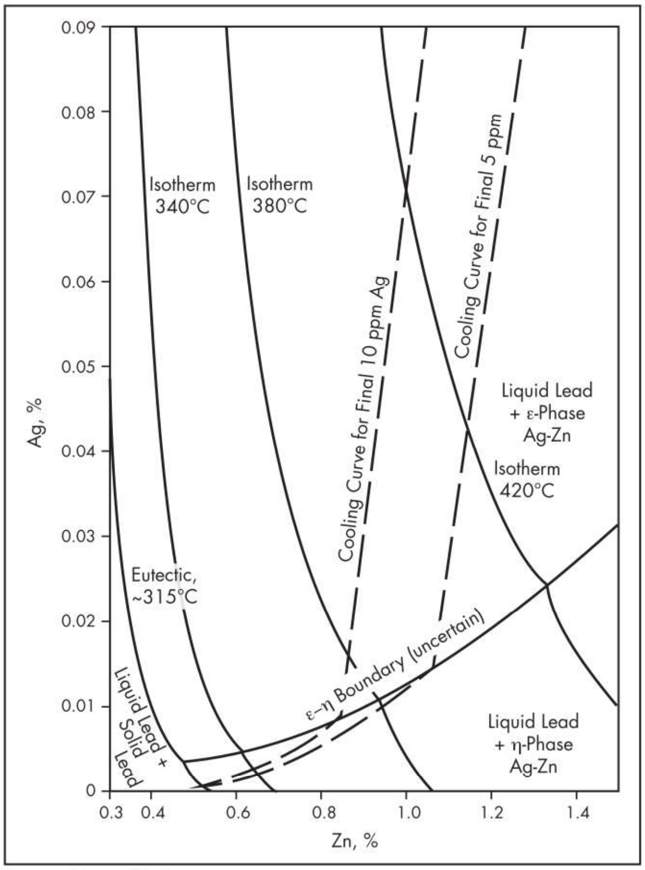
Antimony, arsenic, and tin, which are elements responsible for hardening of lead, are removed from molten lead by oxidation. As those metals are less noble than lead and have a larger affinity to oxygen at elevated temperature, their removal is accomplished by preferential oxidation. Air and/or oxygen is used as the oxidation agent and blown into the liquid lead at temperatures starting around 550°C. Since the oxidation reaction is exothermic, the final temperature of the softened lead may reach 600°–650°C. Generated slag consisting of liquid lead antimony with lead antimonite and lead arsenate containing some solid lead stannate are immediately removed from the kettle by means of a suitable mechanical device due to its aggressive and corrosive nature. The collected slag is solidified and shipped to another plant location to further processing into a marketable lead alloy.

At higher prevailing tin contents, tin is sometimes removed in a separate process step by the addition of ammonium chloride or high chloride containing flue dusts and recovered as a solid dross. With high arsenic and tin levels in the bullion, many smelters are using the Harris process for removal of those metals, plus antimony. This involves treatment of lead with sodium salts (NaOH, $NaNO_3$) at temperatures between 400°C and 500°C, forming sequentially sodium arsenate ($Na_3AsO_4$), sodium stannate ($Na_2SnO_3$), and sodium antimonate ($Na_3SbO_4$). To lower the melting point of the molten salts, a small quantity of sodium chloride is added with the sodium hydroxide. The compounds can be recovered virtually lead free since lead is not converted by this reaction. The produced oxidation products are insoluble but finely dispersed and suspended as fine solids in the molten salt. The molten salt can contain up to 18% As, 20% Sn, and 26% Sb without an increase in viscosity. Other impurities such as selenium and tellurium are also removed from the bullion and report to the molten salts in this process. Although the Harris process has the advantages of lead-free products, no precious metals losses, selective recovery of tin and antimony products, which can be sold and up to 95.5% recovery rate of the sodium salts, it is less and less used in lead smelters because of labor- and cost-intensive treatment of the generated sodium slag, and high equipment cost with high wear rate and maintenance cost.

### *Parkes Process*

The recovery of precious metals (silver, gold) contained in the lead bullion is regarded as one of the most important steps of the entire refining procedure, as the value of the precious metals content in the lead bullion represents a substantial part of the overall metal value. Therefore, it is imperative to minimize the silver and gold amounts bound in the process and to recover them as marketable products as efficiently as possible. Desilverizing is accomplished by the so-called Parkes process and carried out as a two-step process. Silver as well as other precious metals and most residual copper remaining after sulfur decopperizing is removed from the lead by precipitation with zinc as an intermetallic compound.

Lead bullion is pumped from the previous softening step into the desilverizing kettles which already contain crust (low-grade silver–zinc crystals) from the second desilverizing stage. The temperature of the lead bullion is adjusted to about 455°–480°C. The melt is well stirred for about 20–30 minutes so that the lead becomes saturated with zinc. While the molten lead is slightly cooling, Ag–Zn crystals are precipitated and rise to the top together with entangled lead. The formed intermetallic compounds have a higher melting point and a lower specific gravity than the lead and are virtually insoluble in lead saturated with zinc. In this first stage, a so-called "rich" crust is formed and skimmed off the kettle. After removal of the rich crust, fresh zinc as well as recovered zinc from the subsequent vacuum dezincing process and the rich rust treatment is added to the lead bath by stirring. The addition of zinc has to be accurately determined so that the cooling curve crosses the 330°C isotherm above the eutectic concentration of 0.5% Zn (see Figure 21). The charge is transferred to the second stage kettle which contains a quantity of frozen crust from the previous charge. After holding at a temperature of 455°–480°C to melt the crust, the completely dissolved zinc once again forms Ag–Zn crystals in equilibrium with the lead. The crust is then skimmed and returned to the first stage. Desilverizing is completed by cooling the bullion down to nearly freezing at 320°C. Forced cooling of the second-stage desilverizing process is employed to minimize cooling time. A "poor" low-grade silver crust is precipitated out and allowed to freeze on the surface. A slowly rotating mixer is used during cooling, which keeps open a central hole in the crust and also provides sufficient agitation of the lead to prevent freezing of crusts on the kettle walls. This poor crust remains in the kettle being recycled to the next stage desilverizing operation to increase the silver content and also to maintain the maximum throughput for the process.



Source: Davey 1980

**Figure 21 Lead corner in Pb–Ag–Zn system**

The rich silver crust from the first stage of desilverizing contains a substantial amount of entangled lead. Its treatment involves three operations (liquation, dezincing, and cupellation) before either being processed to doré silver in the smelter or sold to a precious metals producer. During liquation, the entire silver-rich crust is melted, whereby it separates into two conjugate layers: the upper one zinc and silver rich, and the lower one rich in lead and comparatively poor in zinc (≈2%) and silver (1%–2%). A flux of borax may be added to prevent atmospheric oxidation, which would hinder the liquation. In the absence of oxides, the crust is melted at 650°–750°C, yielding the low-lead zinc–silver alloy and liquated lead, which is returned to the desilverizing kettles. Liquation is usually carried out in narrow but deep kettles, which are heated preferentially at the top. The rich alloy is dipped from the top while liquated lead is syphoned out from the bottom. Blocks of rich crust are added at intervals and allowed to melt.

The partially de-leaded rich zinc–silver alloy is next subjected to distillation to recover most of its zinc content for reuse. A retort or vacuum induction furnace is employed to distill zinc from the rich alloy. The induction furnace operates in the range of 900°C to 1,100°C. Therefore, it is desirable to retain considerable lead in the alloy so that it does not freeze when most of the zinc has been removed. A clay graphite crucible is contained in a refractory-lined vacuum chamber. The crucible shell is cooled by means of air passed through tubes adjacent to the crucible. The top of the furnace is provided with a water-cooled rubber seal and can be removed for charging. The furnace is connected to the refractory-lined condenser by means of a flanged pipe, which can be disconnected during the tilting of the furnace. The resulting rich silver-alloy ingots are then further treated in a silver refinery in-house for recovering of the precious metals or sold to a precious metals producer. The resulting lead bullion will normally contain less than 10 ppm of silver and is pumped to the next refining step, which is vacuum dezincing (Davey 1980).

#### *Dezincing*

Desilverized lead bullion contains about 0.55% Zn in accordance with the ternary eutectic point in the Pb–Zn–Ag system. This remaining zinc content is usually removed by kinetically controlled vacuum dezincing. A specifically designed kettle incorporating a water-cooled rim is used, which provides the sealing face for the rubber gasket between the kettle and the dezincing unit. The dezincing unit is a circular water-cooled vacuum hood equipped with a rubber gasket around the outer rim. The latter rests on the water-cooled rim. A stirrer is provided for agitating the lead during distillation. The vacuum offtake is through the top part of the kettle, which allows the vacuum pipework to remain permanently connected. The operating cycle consists of a heating stage followed by a distillation stage. The lead is heated from 320°C to the operating temperature of 590°–600°C. The dezincing unit is then positioned and the vacuum pumps started up to adjust an ultimate vacuum of <5 Pa. Up to 95% of the zinc contained in the bullion is condensed on the vacuum bell and recovered for reuse in desilverizing.

Alternative methods of dezincing through either a caustic soda treatment or selective removal with chlorides exist but are not applied anymore because of labor- and cost-intensive operations with lower zinc recovery rates.

#### *Debismuthizing*

After dezincing of the lead, the only impurity remaining is bismuth. Bismuth has a metallurgical deportment very similar to lead and follows the lead almost quantitatively through smelting and refining. The removal of bismuth to concentrations <0.01% can be accomplished through the Kroll–Betterton process. This process, which uses the same principles as de-silvering is typically a one- or two-step procedure, where bismuth is removed through the addition of a lead–calcium alloy and magnesium, a calcium–magnesium master alloy, or a mix of calcium and magnesium scrap. The reagents are added at 420°–480°C while the lead is vigorously stirred. Bismuth is converted to a bismuthide according to the following equation:

$$Ca + 2Mg + 2Bi \rightarrow CaMg_2Bi_2 \quad \textbf{(EQ 29)}$$

The lead is subsequently cooled down to about 330°C. At prevailing bismuth concentrations of 0.05%–0.09% in the lead, a solid crust is formed at the surface with about 1% Bi. The crust is pulled from the kettle and either collected and again treated in a separate kettle with other crusts to enrich the bismuth up to 10% before being sold or treated for bismuth metal recovery. The debismuthized lead undergoes a final refining to remove residual impurities such as tin, arsenic, antimony, and zinc but also calcium and magnesium. This treatment is typically done with caustic soda before the refined lead is cast into ingots or blocks according to required specification or alloyed before casting. Process modifications over recent years have included automation of several of the refining steps, size increases of the refining kettles, improved by-product recovery, and more efficient environmental controls. Research is mainly focusing on the further development of continuous refining methods to improve efficiency and further mitigate environmental emissions.

### Electrolytic Lead Refining

Many different electrorefining technologies have been proposed, but commercially, only electrolytes based on hydrofluosilicic acid, hydroborofluoric acid, or amidosulfonic acid have been employed. Today, electrolytic lead refining with soluble lead anodes is almost exclusively based on the Betts process because of economic reasons. The Betts process is the preferred refining method at bismuth contents in the raw materials of >1% and applied in several lead smelters around the world but predominantly in Asia. It is carried out utilizing a hydrofluosilicic electrolyte containing excess lead fluosilicate to electrorefine impure lead. During the electrorefining operation, the lead anodes are electrolytically corroded with the simultaneous deposition of lead with a higher purity on the cathodes. Electrochemically more noble impurities like silver, gold, copper, bismuth, antimony, arsenic, and germanium are largely retained on the anode scrap as an adherent slime. Less noble impurities like iron, nickel, and zinc will be dissolved at the anode and report to the electrolyte, but their content is usually so low that an enrichment in the electrolyte virtually does not occur. Only tin, with an electrochemical potential close to that of lead (–0.14 V versus 0.126 V) is electrochemically deposited at the cathode together with lead. These advantageous process conditions ensure that even at high impurity levels of the anodes, a cathodic lead with purities higher than 99.99% can be obtained. Furthermore, lead can be refined with a low-energy requirement of about 120 kW·h/kg Pb due to its high electrochemical potential (Gonzalez 2010).

During the electrorefining process, lead is dissolved from the centers of the grains, leaving a skeletal structure of impurities to form the metallic slime layer. Since bismuth forms a solid solution with lead at concentrations normally found in lead bullion, it is imperative for the anode slimes to adhere so that they can cement out the bismuth from the electrolyte after it has corroded with lead. If bismuth does not corrode with lead, it would enrich at the anode surface until lead corrosion is stopped. If insufficient impurities are present in the bullion, in particular antimony, this honeycomb slime layer will be incomplete with low mechanical strength to adhere. The metallic slimes tend to be soft in this case and will often slough off the anodes. Conversely, a high concentration of impurities and here, in particular, copper concentrations >0.05% will result in a very firm, passivating layer that is difficult to remove from the anodes. Therefore, a minimum content of 1.25% of combined antimony, arsenic, and bismuth concentrations in the anode is desired to form a stable and adherent slimes layer.

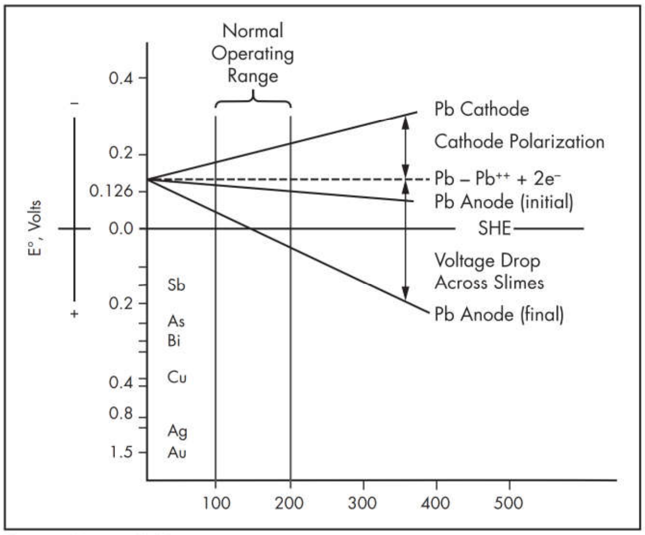
The electrolyte, consisting of 100–185 g/L hydrofluosilicic acid and 60–100 g/L lead as lead fluosilicate, is kept in constant circulation through the cells at flow rates of about 40 L/min. At higher rates, the anode slime can be eroded and cause contamination of the cathodic lead deposit. At much lower circulation rates (<30 L/min), the cathodic deposits become uneven because of insufficient flow, creating adequate electrolyte mixing. Employed current density is adjusted to 120–180 A/m$^2$. The electrolyte temperature is adjusted between 38°C and 43°C. In the absence of additives, lead deposits with a very small overpotential and tends to form rough, porous, or dendritic deposits that result in short circuits. To obtain flat, smooth deposits and minimize short-circuit occurrences, organic reagents (glue and lignin sulfonate) are added to the electrolyte. These reagents increase the cathodic overpotential and change the kinetic parameters and consequently need to be closely monitored.

The anodes are cast at a thickness between 18 and 25 mm based on the prevailing bismuth content and replaced typically in 6–8-day intervals to limit the anode corrosion period and prevent the voltage drop across the adhering slime layer from exceeding a critical value above which impurities dissolve and contaminate the cathodic deposit. Cathodes are produced from electrolytically refined lead with a thickness between 0.8 and 1 mm. They are manufactured by means of submerging a water-cooled rotating drum in a molten lead bath. One cathode cycle is typically 4–8 days.

To prevent current losses and to maintain the electric power consumption at high current efficiencies and cathode quality, it is important to closely monitor cell voltage and operate at minimum levels. The electrochemistry of the process is illustrated in Figure 22. This graph shows the operating potentials as a function of current density and time. The cell voltage tends to slightly increase during the duration of the refining cycle. Besides the voltage of the electrodes' contact and resistance, main contributors to these voltage changes are the slime resistance voltage and the electrolyte voltage. The Betts process depends on the formation of adherent, porous anode slimes. The slime layer formed undergoes structural and chemical changes during its growth, resulting in a voltage increase. In addition, the resistance of the electrolyte contributes significantly to the increase in voltage during the refining cycle because of a loss in free acid. A control value at 90 g/L or higher for the free acid concentration in the electrolysis is set and maintained. For steady operation at 160–180 A/m$^2$, the cathode overpotential is controlled at about 90 mV. The anode overpotential with new anodes is about 10 mV, and the plating cycle must end when the anode overpotential reaches 200 mV above the reversible potential for lead. At this point, the anode potential is also within 200 mV of the more positive bismuth potential. To avoid dissolving bismuth at the anode, the anode potential must not exceed +0.76 V (SHE, or standard hydrogen electrode) or 200 mV anode overpotential. From the diagram, it is obvious that some antimony will contaminate the cathodic lead deposit at that potential.

Overall current efficiencies of 98% are obtained in the Betts process. However, the slightly higher current efficiency at the anode compared to the cathode results in a lead accumulation in the electrolyte. Therefore, a bleed of the electrolyte is frequently sent to a lead removal tank where the lead in the electrolyte is precipitated as lead sulfate crystals by adding sulfuric acid or recovered in metallic form through an electrowinning process. The clarified de-leaded solution flows into a bismuth removal tank filled with lead shot where bismuth is removed by cementation before it returns to the electrolyte circuit.

During the electrorefining operation, fluosilicic acid is consumed by entrapment in the anode slimes and by volatilization from the surface of the electrolyte. The acid develops significant vapor pressures through the volatile decomposition products HF and $SiF_4$. Both are corrosive and toxic and are removed from the cellhouse atmosphere by adequate ventilation.



Source: Krauss 1990

Figure 22 Betts process electrochemistry

The slimes from the used and corroded anodes are removed through the application of scrapers, mechanical brushes, or the impact of high-pressurized water. The cleaned scrap anodes with a remaining weight of about 30% of the original anodes are returned to the smelter while the slimes are collected and transported for further treatment. The slimes, representing only 4%–5% of the anode weight, can be treated by a variety of processes to recover silver, gold, antimony, copper, bismuth, and sometimes tin and indium. The lead cathodes are washed, melted, and cast into ingots or blocks after removing residual tin and antimony through a caustic treatment.

## BISMUTH

### Mineralogy and Occurrence

The bismuth contents in the earth's crust are estimated to be 0.2 ppm. Elemental bismuth may occur naturally in up to 99% Bi purity, although its sulfide ($Bi_2S_3$ with 81.3% Bi), oxide ($Bi_2O_3$), and bismutite ($nBi_2O_3 * m\ CO_2 * H_2O$) form important commercial ores.

The total number of minable ore deposits is low, and only a small amount of bismuth ores are economically processed to metal. Bismuth minerals are predominantly extracted as by-products from copper, lead, tin, tungsten, molybdenum, cobalt, nickel, silver, and gold ores. Significant amounts of bismuth are recovered from anode sludge generated during copper and lead electrorefining as well as bismuth crust from the pyrometallurgical refining of lead or flue dusts and precipitation products. The largest bismuth deposits can be found in Bolivia, China, Spain, and Peru, where significant amounts of bismuth are recovered from intermediate products during the metallurgical recovery of copper, lead, and tin.

### Properties

An overview of the most important properties can be found in Table 8. Bismuth is a pentavalent post-transition metal and chemically resembles arsenic and antimony. It is a brittle metal with a silvery white color when freshly produced but

**Table 8 Properties of bismuth**

| Property | Units |
|---|---|
| Atomic mass | 208.98 |
| Density, g/cm$^3$ | 9.78 |
| Melting point, K | 544.98 |
| Boiling point, K | 1,837 |
| Heat of fusion, kJ/mol | 11.3 |
| Heat of vaporization, kJ/mol | 151 |
| Heat capacity (25°C), J/(mol*K) | 25.52 |
| Electrical resistivity (20°C), μΩ*m | 1.29 |
| Thermal conductivity (300 K), W/(m*K) | 7.97 |
| Thermal expansion (25°C), μm/(m*K) | 13.4 |
| Brinell hardness, MPa | 94.2 |

Source: Kammel 1989

is often seen in air with a pink tinge, owing to surface oxidation. Bismuth is the most naturally diamagnetic element and has one of the lowest values of thermal conductivity among metals. The electrical resistance of solid bismuth is larger than that of its liquid phase. When deposited in sufficiently thin layers on a substrate, bismuth is a semiconductor, despite being a post-transition metal (Kammel 1989).

Elemental bismuth is denser in the liquid phase than the solid, a characteristic it shares with antimony, germanium, silicon, and gallium. Bismuth expands 3.32% on solidification; therefore, it was long a component of low-melting typesetting alloys, where it compensated for the contraction of the other alloying components to form almost isostatic bismuth–lead eutectic alloys. It needs to be emphasized that bismuth, unlike most other metals, solidifies with a volume increase of 3.32%. Bismuth is more noble than lead and does not really react with air, water, and nonoxidizing acids. With nitric acid, it reacts forming nitrogen oxide, while sulfuric acid dissolves it to bismuth sulfate while generating sulfur dioxide. At elevated temperatures, the metal instantly reacts with halogens and sulfur. Its compounds tend to hydrolyze in aqueous solutions at a pH > 0.5.

The recovery of bismuth from ores, concentrates, or other raw materials is predominantly carried out by means of roast reduction technology, or precipitation or segregation processes. Because of the low solubility of bismuth compounds in aqueous solutions, the application of hydrometallurgical processes is only used for the treatment of intermediate products or waste products, the enrichment of low-bismuth-bearing raw materials, or for the removal of other metals. To recover bismuth, a mixture of sulfides, oxides, metallic bismuth-containing ores, and intermediate products is typically treated because of the limited availability of one single raw material. All pyrometallurgical processes are conducted at relatively low temperatures to minimize higher evaporation losses due to the high vapor pressure of metallic bismuth and bismuth sulfide at elevated temperatures. In addition, the extremely varying compositions of the different ores and intermediate products demand that each smelter adapt the applied process technology to the special requirements of the treated raw materials.

## Enrichment of Raw Materials

The pyrometallurgical recovery of bismuth is only economical with raw materials containing more than 10% Bi. The low metal content in most bismuth ores requires mechanical processing in aqueous solutions or flotation to increase the metal concentration. If these technologies are not viable methods, it is possible to increase the metal content through distillation or precipitation from aqueous solutions. This applies particularly for bismuth containing flue dusts but also to treat low-bismuth-bearing oxides. In precipitation technology, the bismuth is dissolved through leaching with concentrated hydrochloric acid. From the resulting chloride solution, bismuth is precipitated either with iron or it is precipitated by means of hydrolysis as oxychloride as follows:

$$BiCl_3 + H_2O = BiOCl + 2HCl$$

The precipitation step in this process technology can be accomplished through dilution with water or through the addition of soda or milk lime. The majority of the bismuth separation is already completed at a pH value of around 2 with <1 g/L Bi remaining in solution.

## Crude Bismuth

The roast reduction process is the most common extraction process and is considered for sulfidic and sulfide-oxide ores, which are jointly molten under reducing atmosphere to crude metal after calcination at moderate temperatures.

The melting of the calcine generated from oxychlorides or other oxidic raw materials takes place in a reverberatory furnace or a crucible furnace with the addition of soda, lime, fluorspar, and recirculated slag that returns to form low-melting slag. Carbon to adjust a reducing atmosphere is added between 3% and 6% of the charge. Since the roasting of ores is incomplete at low temperatures, iron turnings are added for converting the remaining $Bi_2S_3$ that had not reacted during the roasting process. Simultaneously, this also converts arsenic and antimony, forming a speiss. When processing the bismuth-bearing materials in a reverberatory furnace, the new feed material is charged into the liquid slag and initially melted only at moderate heat under a reducing flame. Only after complete reduction has been accomplished is the operating temperature increased to tap and discharge the weak acidic alkaline silicate slags in a liquid form with very low viscosity. Because of the extremely low viscosity of the slag and the low melting point of the crude bismuth, the process is carried out in a refractory-lined and mobile furnace similar to the type of the English (Treib) furnace, which can be easily replaced. In smelters with small throughput capacities, crucible furnaces are employed as the preferred equipment. These furnaces are installed in a ring-type arrangement. The crucibles are constructed from refractory clay mixed with about 20% graphite. Although the operating costs of this technology are higher, the overall evaporation losses are less than in a reverberatory furnace, resulting in higher yields.

The recovered crude bismuth from the roast reduction process is further refined to bismuth metal. Simultaneously generated matte with typically 5–8% Bi is ground, roasted, and in most cases its bismuth content is further enriched through a hydrometallurgical treatment. If the slag from the refining process contains bismuth in concentrations larger than 0.1%, it is recirculated to the smelting step. Otherwise, it is disposed to an appropriate landfill.

In precipitation technology, crude bismuth is recovered from sulfidic raw materials by adding iron turnings with the following reaction taking place:

$$Bi_2S_3 + 3Fe = 2Bi + 3FeS$$

Although this technology has the advantage of not requiring a roasting step, it was almost completely replaced by the roasting process under reduced atmosphere because of the substantial amount of co-generated matte. Today, it is exclusively applied for processing $Bi_2S_3$ ores or ores that are rich in copper, arsenic, and antimony. The precipitation technology is mostly performed in crucibles, which produces a matte with low bismuth contents. It is required to add sodium sulfate, gypsum, soda, and coal as flux reagents and fuel to the overall process.

Bismuth-bearing by-products from lead refineries are most often initially reduction treated to form a lead–bismuth alloy. This is followed by either a selective oxygen, sulfur, or chloride treatment. Alternatively, the lead–bismuth alloy can be leached with hydrochloric acid or electrolytically concentrated in the anode sludge during the lead electrolysis. Subsequently, the products are oxidized in a converter where bismuth reports to the slag. Crude bismuth is then generated from the slag in a smelting step under reducing atmosphere.

## Refining of Crude Bismuth

The bismuth contents of crude bismuth and bismuth-enriched alloys are varying and can contain up to 70% Bi. The preferred refining methods are pyrometallurgical processes. On one hand they are more flexible and allow the treatment of more impure crude bismuth or bismuth alloys, and on the other hand they also produce final bismuth metal with higher purity. The application of electrorefining demands a bismuth metal high in bismuth (>97%) and low in arsenic, antimony, and copper, which is then cast into anodes.

The process steps in the pyrometallurgical refining of bismuth are comparable to the refining of lead bullion. Copper is removed by stirring sulfur or sulfur-containing additives into the melt at temperatures between 400°C and 500°C. Subsequently, arsenic and antimony are decreased to levels of 0.1 ppm through the addition of sodium hydroxide. Precious metals are removed in accordance to the Parkes process as a foam. Compared to this refining step for lead, the required amounts of zinc are higher with about 12.5 kg $Zn/t_{metal}$ or 2 kg Zn/kg Ag. Zinc and lead are removed through the injection of chlorine gas or stirring chlorides into the melt.

By looking at the standard reduction potential for the elements, it is obvious that only lead and silver can be effectively removed of all the prevailing impurities from bismuth ($Bi/Bi^+ = +0.2$ V) in the electrorefining process. Other impurities such as, for instance, antimony ($Sb/Sb^{3+} = +0.24$ V) are co-deposited at the cathode. Copper is collected partly in the anode sludge but, to some extent, also dissolved and reduced at the cathode. Therefore, it necessary to virtually remove all the copper, antimony, and arsenic in a pyrometallurgical refining step prior to electrorefining for the recovery of bismuth with high purities. Electrorefining of bismuth is mainly carried out in $BiCl_2$—solutions with about 100 g/L Bi and 100 g/L free hydrochloric acid. During the electrorefining process, which is performed at ambient temperature and with a current density of about 130 A/$m^2$, the top of the electrolyte is covered with a layer of oil or paraffin to prevent oxidation of copper and iron. The cell voltage of electrolysis is, at a maximum, 0.1 V. At elevated levels of antimony or lead in the anode, a diaphragm is employed. A silver plate is used as a permanent cathode sheet. This ensures that the brittle bismuth deposits can be easily stripped from the cathode. The generated anode sludge may contain up to 40% Bi.

Alternatively, an electrolytic refining process employing a hydrofluosilicic acid solution is used. In this process a copper blank is used as a permanent cathode sheet. The anodes are covered with anode bags made of polypropylene. The electrolyte contains 40 g/L Bi and 330–350 g/L of free hydrofluosilicic acid. In addition, 1 g of glue is added per ton of bismuth produced. The electrolysis is operated at a current density of 60 A/$m^2$, at which the cell voltage is about 0.2 V and current efficiencies of up to 93% can be accomplished. The anode and cathode cycle is commonly 8 days, after which the anode scrap is about 50%–55% and the anode slime rate is about 0.4%.

In both electrorefining methods, the sludge from the anode scrap will be removed by mechanical scraping. The collected high-silver-containing anode sludge is typically treated further to recover the silver, while low-silver-containing anode sludge is recirculated for anode production. The scrap anodes are further washed before being returned to the melting kettle for recycling.

After washing with water, the electrolytic bismuth is stripped of the cathodes manually or in an automated stripping machine. The cathode blanks are returned to the electrolytic cells while the refined bismuth is melted in a kettle, cleaned by a caustic soda treatment, and cast into ingots by a continuous casting machine. The refined bismuth metal typically has a purity of >99.99%. This is sufficient for the production of bismuth compounds. The production of pharmaceutical products demands bismuth that is free of arsenic, lead, and tellurium, at purity levels of >99.99%. Ultrapure bismuth of 99.9999% purity is used for the semiconductor and nuclear industry. This requires a subsequent refining step, which can be either zone melting or vacuum distillation.

Bismuth compounds account for about 60% of the production of bismuth. They are used in cosmetics, pigments, and a few pharmaceuticals, notably Pepto-Bismol, used to treat diarrhea. Bismuth's unusual propensity to expand upon freezing is responsible for some of its uses, such as in casting of printing type. Multiple-component alloys with cadmium, indium, lead, tin, and tellurium are characterized by melting points as low as 47°C. In conjunction with the unusual contraction (at bismuth contents of <47%) and expansion (at bismuth contents of >55%) properties, these alloys are also used as casting cores and forms as well as solder materials. As a metal, it is not used in many applications because of its poor mechanical properties, except for electrodes in pH measuring units, thermostat liquids for high-temperature applications, heat exchanger fluids, and catalysts. In addition, bismuth has unusually low toxicity for a heavy metal. As the toxicity of lead has become more apparent in recent years, there is an increasing usage of bismuth alloys (presently about one-third of bismuth production) as a replacement for lead. Bismuth compounds such as bismuth chloride are used as pigments, while bismuth trioxide is used as a pigment but is also used in the porcelain industry (Kammel 1989).

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