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promulgated a workplace standard of 50 μg/m^3 per 8 hour exposure and a blood level standard of 40 μg/100 ml of whole blood. Operation and maintenance (O&M) techniques will become important tools in maintaining continued compliance with standards.

The prevention of lead emissions from secondary smelters will be shown to depend largely on O&M practices. Fabric filters are usually used to remove particulate matter from lead smelter process and ventilation gas streams. Because properly operated fabric filters are very efficient, little lead particulate matter is emitted in stack gases. Fugitive emissions, however, are a major problem. Control systems are only partially effective in capturing fugitive emissions. Also, handling of the lead particulate matter after it has been collected is a potential cause of fugitive emissions. Lead dust escapes from the materials handling and smelting processes into the workplace and is continually reentrained and dispersed throughout the smelter. Sufficient reentrainment may occur to cause the NAAQS of 1.5 μg/m^3 to be exceeded. Continued compliance can be achieved only by applying the appropriate combination of engineering and administrative controls, and by adopting operating, maintenance, and housekeeping practices to make those controls work effectively.

Inspection & operating & maintenance guidelines for sec. lead smelter air pollution control. (Final Rept)/ F. Hall, ET al. Pedco-Environmental, inc Cincinnati OH Jan 8.

PB 84-149.368

SECTION 2

DESCRIPTION OF PROCESSES AND OPERATIONS

The secondary lead industry is relatively complex in that a number of processing steps are combined in various sequences to produce seven principal products. Figure 1 is a generalized flow diagram for secondary lead smelting. There are three basic process steps at a secondary lead plant: pretreatment, smelting, and refining. One or more furnace types (blast, reverberatory, and kettle) are used in each process; the furnace combinations selected depend upon the type of scrap processed and the desired product mix. These operations and the associated equipment are discussed in this section.

2.1 PRODUCTION PROCESS OVERVIEW

As shown in Figure 1, a secondary lead plant processes lead bearing materials such as automotive batteries and battery plates, battery manufacturing scrap, rerun blast furnace slag, reverberatory furnace slag, dross, flue dust, and scrap lead metal (e.g., pipe and flashing) to produce lead products of varying hardness, lead oxides, and lead alloys.

2.1.1 Pretreatment

The lead-bearing raw materials are commonly stored outdoors in large piles and are transported around the smelter in front-end loaders and/or trucks (Figure 2). These materials usually must be processed in some way before they can be fed to the smelting furnaces. For example, batteries are decased or crushed; some feed materials are subjected to sweating to recover lead and lead alloys with low melting points; battery plates and scrap may be premelted before charging to the smelting furnace; and collected flue dust and dross may be agglomerated before recycling.

Preparation of whole batteries for decasing varies. Incoming batteries are segregated by battery case material (e.g., plastic or rubber). The batteries are usually cut by a saw or a shear in an enclosure for removal of battery tops and posts, but some are crushed on the ground by a track bulldozer. The acid is drained from the batteries, and the lead plates, posts, and intercell connectors are removed from battery cases, collected, and stored in a pile for charging to the process furnaces.

In the sweating operation lead and lead alloys with low melting points (e.g., solder, babbitt) are selectively melted and separated from pieces of scrap iron, copper, or aluminum which remain behind intact. Radiators, cables, bearing housings, and various items of soldered or lead-covered scrap are

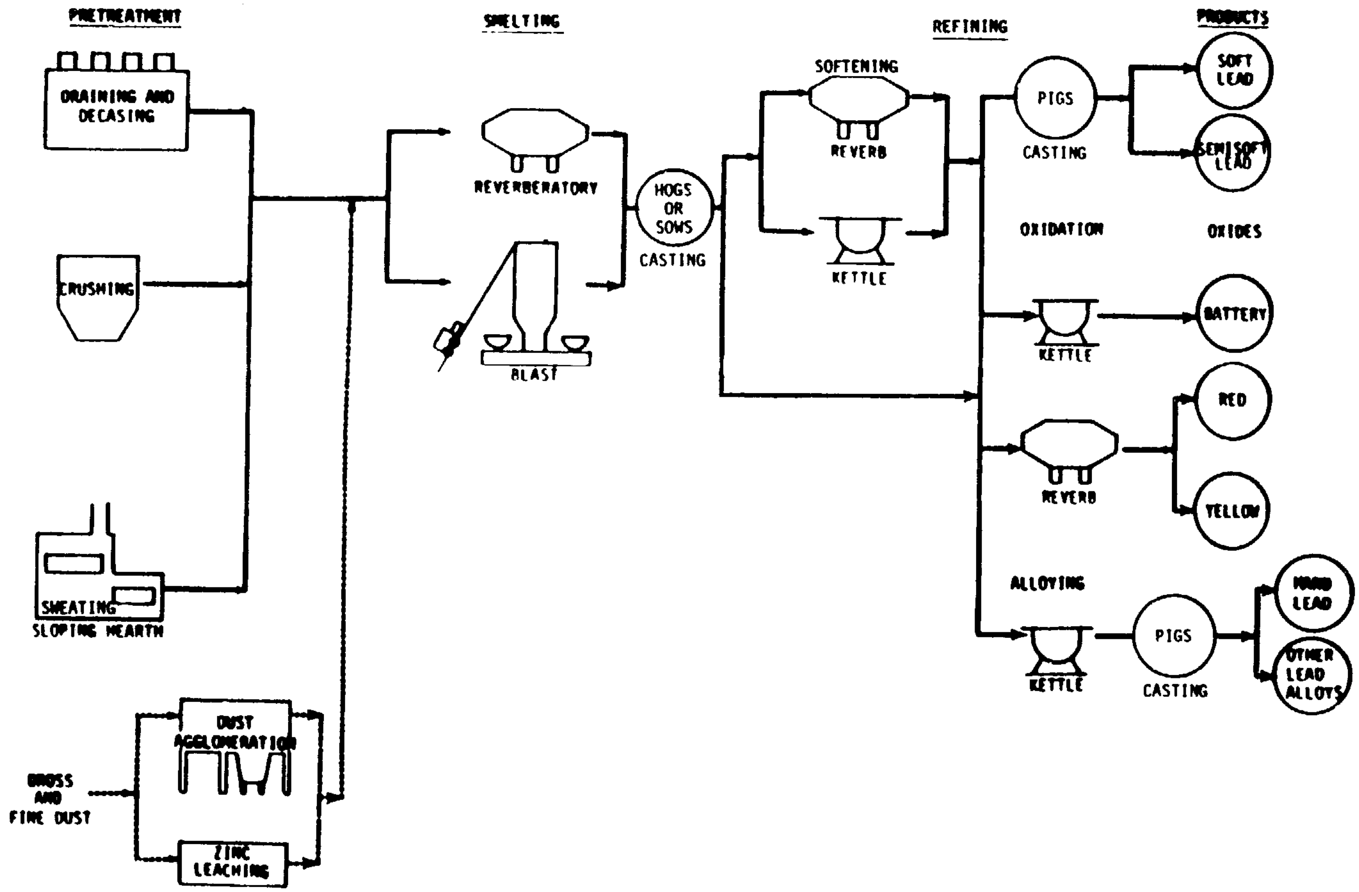


Figure 1. Secondary lead process flow diagram.

Figure 2. Front-end loader transferring batteries.

typical feed materials. Sweating is performed in direct gas or oil fired reverberatory or rotary furnaces. Reverberatory furnaces are typically used to process high lead content scrap and rotaries usually process low lead content scrap.

One smelter melts battery plates and battery manufacturing scrap before the scrap is smelted in a blast furnace. The melted scrap is tapped from the furnace and allowed to cool into slag-like chunks. These chunks are reported to be an ideal feed material for the blast furnace and allow rapid smelting.

Fabric filter dusts from reverberatory, rotary, and blast furnaces and from kettles are remelted and agglomerated at many secondary lead smelters. The agglomerated product allows better lead recovery by the smelting furnaces and decreases fugitive emissions.

Other pretreatment operations may include crushing large pieces of scrap with a jaw crusher to reduce the scrap to a suitable size and zinc leaching to dissolve zinc from collected reverberatory furnace flue dust to reduce the zinc concentration in the blast furnace feed. After the pretreatment operations, the lead-bearing materials are processed by the smelting furnaces.

2.1.2 Smelting

Smelting produces a purified lead by melting and separating lead from metal and nonmetallic contaminants and by reducing the oxides to elemental lead. This is accomplished by exposing the furnace charge materials to a reducing atmosphere at a temperature of about 950°C (1750°F) so that the oxides can be reduced and the sulfur and waste oxide components (silicon dioxide, iron oxide, and others) can be removed as slag. Smelting is carried out in blast furnaces, reverberatory furnaces, and rotary furnaces.

Hard or antimonial leads containing about 10 percent antimony are commonly produced in the secondary lead industry by blast furnaces (sometimes called cupolas or shaft furnaces). Pretreated scrap metal, coke, rerun slag, recycled dross, flue dust, scrap iron, and fluxes (e.g., limestone) are used as charge materials to the furnace. The process heat needed to reduce the lead components of the charge to metallic lead is provided by the reaction of the charged coke with blast air that is blown into the furnace.

Semisoft lead products that contain 3 to 4 percent antimony are commonly produced in reverberatory furnaces, but can also be produced by rotary kiln furnaces (rarely used in the United States). The lead is produced using metallic battery parts, oxides, drosses, and other residues. This charge is heated directly using either natural gas, oil, or coal.

2.1.3 Refining

Refining and processing the crude lead from the smelting furnaces can consist of softening, alloying, and oxidation depending on the final products desired. These operations can be performed in reverberatory furnaces (discussed earlier) or kettles, but kettles are most commonly used.

Intermediate smelting products, especially from blast furnaces, may contain antimony or copper; either element makes the lead hard. Kettles are used for softening processes to remove these contaminants and thus produce a soft lead product. The process steps consist of charging the preheated kettle; melting the charge; agitating the flux into the molten charge; skimming the drosses; and pouring or pumping the molten metal. In some cases, molten lead is charged directly from the smelting furnace into the refining kettle. Often, separate kettles are used to remove various impurities.

Refining furnaces remove copper and antimony to produce soft lead and remove arsenic and nickel to produce hard lead. Sulfur can be added to reduce copper content while aluminum chloride, sodium nitrate, sodium hydroxide, and air can be used to reduce antimony content. Aluminum chloride also removes nickel.

Alloying furnaces are used to melt and mix ingots of lead and alloy material. Antimony, tin, arsenic, copper, and nickel are the most common alloying materials.

Oxidizing furnaces are either kettle or reverberatory furnaces which oxidize lead and entrain the product lead oxides in the combustion air stream. The product is subsequently recovered in baghouses.

Kettles are also used to remelt final products for casting.

2.2 PROCESS OPERATIONS

This section presents a more detailed description of the operation of a secondary lead plant.

2.2.1 Pretreatment

Battery Handling--

Preparation of whole batteries for decasing varies. Incoming batteries are segregated by battery case material (e.g., plastic or rubber). The batteries are usually cut by a saw or a metal shear in an enclosure for removal of battery tops and posts (Figure 3), but batteries are also crushed in the open by a track bulldozer. Then the acid is drained from the batteries, and the lead plates, posts, and intercell connectors are removed from battery cases and stored in a pile for charging to the process furnaces. The drained acid passes to a sump, and the stored plates are sprayed with water to remove any retained acid. This acid has a pH of about 0.6 (Mezey 1979). The acid in the sump is neutralized with lime before it is discharged to a holding pond or sewer system.

Figure 3. Battery decasing.

Empty battery cases and battery tops can be washed and shredded for landfill or resale. Some smelters use battery cases in the blast furnace as a portion of the fuel. The charge is premixed to maintain a uniform material mixture in the furnace and control furnace temperatures. Because vulcanized rubber cases can be a source of sulfur resulting in sulfur dioxide emissions, they are normally removed and discarded to minimize generation of sulfur dioxide emissions in the smelting operation. From European experience, smelters which feed PVC plastic battery cases to blast furnaces on a continuous basis and recycle collected dust must eventually remove the lead chloride which builds up in the furnace by leaching (Burton et al. 1980).

Sweating--

The feed materials for a secondary lead smelter typically contain various items of soldered or lead-covered scrap derived from radiators, cables, and bearing housings. In addition to the lead, the scrap contains higher melting metals such as iron, copper, and aluminum components which are undesirable in the smelting and refining stages. These undesirable components are separated from the lead components through a process termed sweating. Sweating is a physical separation of metals based upon melting points. In the secondary lead process the scrap is heated in a direct-gas or oil-fired furnace of the reverberatory or rotary type.

Reverberatory furnaces are typically used to process high content lead scrap such as battery plates, and rotary furnaces are usually used to process low content lead scrap (lead-sheathed cable and wires) type metal drosses. The furnace is operated at temperatures 340° to 540°C (650° to 1000°F) above the melting point of the lead alloys and below those of the undesirable metals.

A sloping hearth type of reverberatory furnace (illustrated in Figure 4) is the most common furnace used for sweating. The scrap pieces are pushed or dumped onto the furnace hearth either by hand or with a mechanical loading device. After the metals melt and flow down the hearth, the furnace operator rakes the pieces of unmelted scrap off the hearth and out of the furnace. These scrap pieces may be sold to foundries or to secondary copper and aluminum smelters for recovery of the remaining metals. Hoes and rakes are used to

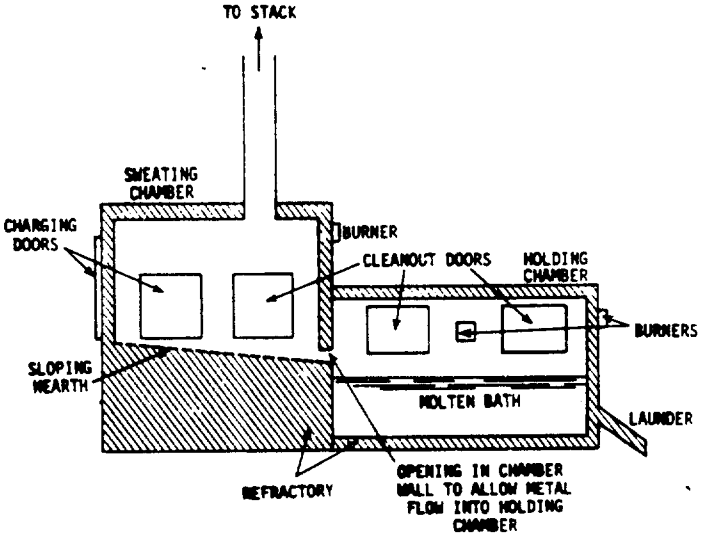


Figure 4. Sloping hearth sweating furnace.

remove the scrap through access doors. When a rotary kiln sweating furnace is used, the scrap falls into a bin at the end of the furnace. The lead or lead alloys are collected in a well or a holding kettle furnace. The metal can then be cast or pumped to other furnaces for further processing.

Agglomeration--

Several secondary lead plants remelt and agglomerate fabric filter dusts from operating furnaces to allow better lead recovery and decrease fugitive emissions (Section 3). Where agglomeration is not practiced, flue dusts may be recirculated directly to either the smelting blast furnace or reverberatory furnace or stored for a later lead recovery. A large amount of this dust is entrained in the furnace flue gas system and must again be collected by the control system. If the flue dust is stored before recycling, the dust particles can become windblown and add to plant fugitive emissions. The agglomeration process (Figure 5) melts the flue dust and fuses the particles together

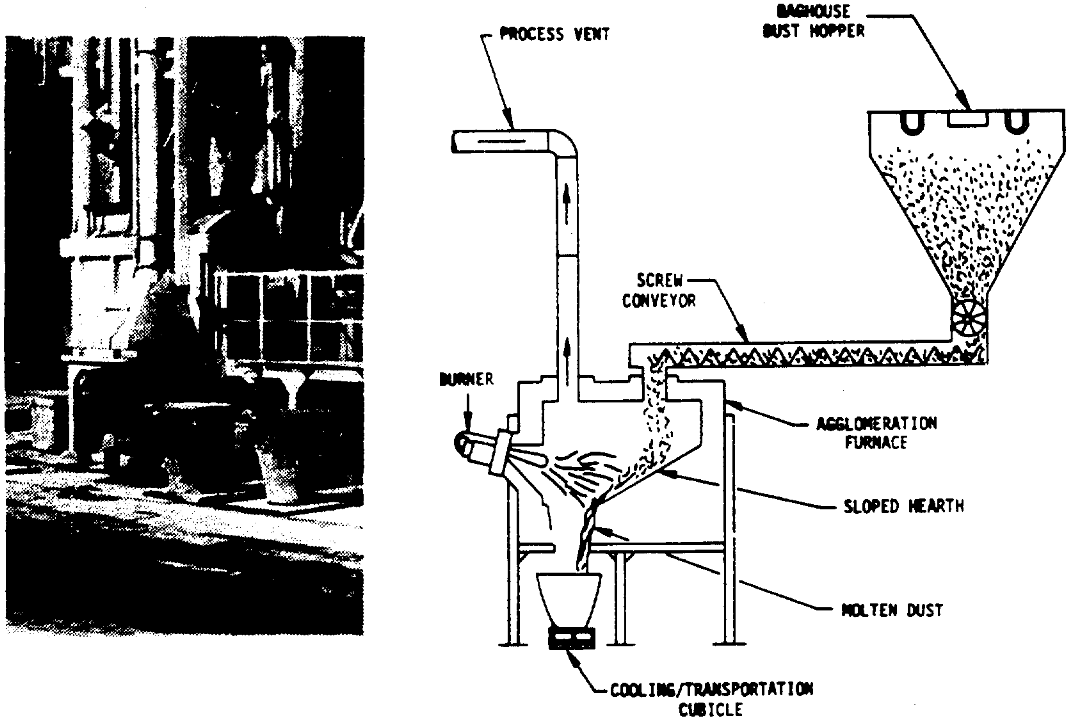


Figure 5. Flash agglomeration furnace (Coleman and Vandervort 1980).

to form a large solid piece of material in the shape of the receiving vessel. Tipping the solidified contents of the vessel on the ground is usually sufficient to break the material into lumps small enough for recharging to the smelting furnace and large enough to prevent entrainment in the furnace flue gas system. Since less flue dust is generated and because the volume of recycle material is reduced by approximately 80 percent, additional lead bearing material can be charged to the furnace which increases the smelting rate. Blast furnaces that smelt battery scrap generate dusts that are amenable to agglomeration. Some dusts, however, that contain zinc or copper cannot be processed in such a furnace either because their melting points are too high or because they raise the melting point of the mixture above the operating temperature. The agglomerated material is a suitable blast furnace feed. It can also be used as a detinning agent in kettle refining. Agglomeration, however, may not be applicable if the dust is not recycled to the blast furnace, if the chlorine content of the dust is too low, if the smelting furnace afterburner is not operating properly, or if the furnace top temperatures are high enough to vaporize a significant quantity of metallic lead.

Figure 6. Agglomerated dust plug.

Recently published reports (Schwitzgebel 1981, Mackey and Bergsoe 1977, Coleman and Vandervort 1980, Coleman and Vandervort 1979) differ about the applicability of dust agglomeration to flue dusts from secondary lead smelters. Available data indicate that smelters differ widely in the type of scrap they use and in their operating practices. Research is required before a recommendation can be made about the use of flue dust agglomeration in a reverberatory furnace by any specific smelter. Flue dust reverberatory furnaces are in use in U.S., and are similar to agglomeration furnaces. Items to consider include:

- Dust composition, melting point, and generation rates
- Fluctuation in dust production rates
- Afterburner performance
- Recycle practices
- Changes in furnace feed materials
- Furnace temperature control

Furnace operating temperatures depend on the dust composition. Temperatures ranging from 399° to 898°C (750° to 1650°F) are the most likely operating points for agglomerating dusts generated from battery scrap smelting.

2.2.2 Smelting

Blast furnaces, reverberatory furnaces, and rotary furnaces can be used for smelting. Reverberatory smelting furnaces are used to produce a semisoft lead product that typically contains 3 to 4 percent antimony. Blast furnaces produce hard or antimonial lead containing about 10 percent antimony. Rotary kiln furnaces are occasionally used for smelting in the United States but can produce lead products similar to those produced in reverberatory furnace.

Blast Furnaces--

Blast furnaces (sometimes called cupolas or shaft furnaces) are commonly used for smelting in the secondary lead industry. The furnaces are refractory-lined, water-cooled, steel vessels, usually open at the top. Pretreated

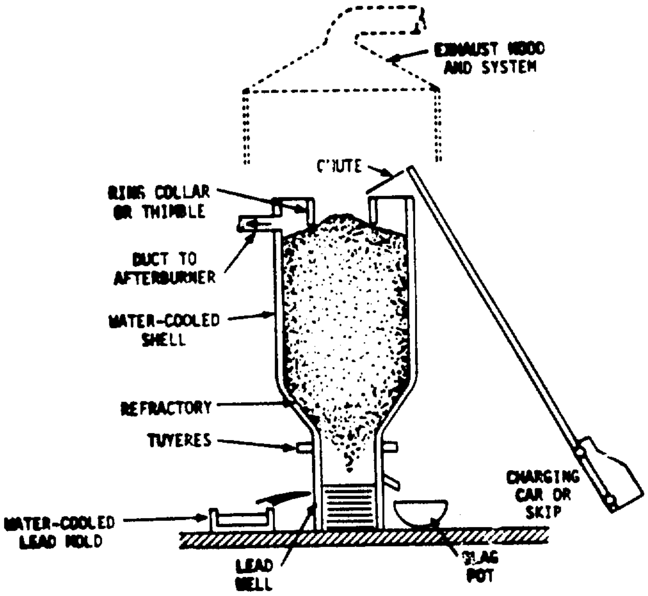


Figure 7. Open top blast furnace.

scrap metal, coke, rerun slag, recycled dross, flue dust, scrap iron, and fluxes (e.g., limestone) are charged into the furnace either in alternate layers or as a mixed feed. Charging devices that may be used, include skip hoists, conveyor belts, and front-end loaders (Figure 8).

The first step in blast furnace smelting is charging. A typical blast furnace charge contains 55 to 87 percent battery scrap; 7 to 20 percent drosses, oxides, leaching residue, and reverberatory slag; 5 to 8 percent coke; 2 to 6 percent rerun slag; 1 to 6 percent scrap iron; 1 to 3 percent flue dust; and 1 to 5 percent limestone. Lead drosses contain antimony, copper, caustic, and other residues from the refining processes. Reverberatory slag may contain lead, silica, tin, arsenic, copper, and antimony. Rerun slag is a highly silicated slag tapped from previous blast furnace runs. Not all blast furnace slag is necessarily recycled.(Iron and limestone form an oxidation-retardant slag that floats on top of the melt to prevent oxidation of the reduced lead in the smelting furnace.)

Blast air (sometimes oxygen-enriched) is introduced through tuyeres just above the slag level in the furnace. The air reacts with coke in the charge to produce heat, carbon monoxide, and carbon dioxide. The hot gas rises through the charge material in the furnace, preheats it, and provides the necessary reducing atmosphere for smelting. Smelting occurs at the tuyere level, where carbon and carbon monoxide reacts with lead sulfates, oxides, and carbonates to form lead, sulfur dioxide, and carbon dioxide. Temperature at the tuyere level is approximately 1010°C (1850°F).

Figure 9. Blast furnace tuyeres and slag tap.

Furnace slag floats on top of the lead in the furnace and is tapped intermittently from a hole that is drilled through the furnace refractory that is located at a higher level than the lead tap hole and usually 180 degrees from the lead tap hole. The hole is then sealed with a fire-clay plug after the slag is tapped. The furnace slag level is monitored by removing the tuyere covers, peering through glass inserts in the tuyere covers, checking the tuyere air pressure, timing previous slag taps, or a combination of these techniques. At no time should the slag level be allowed to rise above the tuyere level. Quite often, rods must be inserted through the tuyeres to clean slag accretions that form when slag splashes the tuyeres. This is commonly referred to as "punching the tuyeres."

Slag is usually tapped into crucibles for cooling (Figure 10). If enough iron is present in the furnace charge, a liquid called matte, which consists

Figure 10. Slag tapping crucible.

of lead, iron, and sulfur, forms at the bottom of the slag crucible. Matte differs from slag and lead bullion. Most of the sulfur (95 to 98 percent) in the feed material accumulates in the matte or slag/matte mixture. The matte can be broken from the slag when the slag crucible is cooled and dumped. Thus, the slag, with its higher lead content, can be charged to the blast furnace without recycling most of the sulfur. Not all the slag, however, is necessarily recycled.

Molten lead settles to a lead well at the bottom of the furnace. Normally, it is continuously tapped from the lead well through a hole in the furnace wall. The temperature of the molten lead is 871° to 898°C (1600° to 1650°F). Next, the lead is fed by gravity via a runner into a water-cooled mold or a holding kettle where the temperature is 371° to 538°C (700° to 1000°F). The crude lead is then cooled and cast into 227-kg (500-lb) sows or into hogs, which range from 680 to 1360 kg (1500 to 3000 lb).

Figure 11. Lead tapping.

Additional limestone can be added to the furnace to reduce the lead content of the ferrosilicate blast furnace slag. This addition, however, raises the melting point of the slag mixture, which contains silicon oxide (SiO_2), ferrous oxide (FeO), and calcium oxide (CaO). Adding extra limestone also increases slag viscosity, so that the slag is sticky and difficult to remove from the furnace. Oxygen lances can be used to heat such slag and make it flow. Extreme care must be taken, however, to prevent overheating of the refractory, causing hot spots and ultimately, a sudden furnace rupture. This is particularly critical where water cooling is used to prevent the possibility of water contacting hot metal, resulting in a "metal explosion" from the rapid steam generation.

Blast furnace capacities range from 15 to 40 Mg (16 to 44 tons) of lead/day per square meter of furnace cross section. The operating capacity is usually limited by the amount of gas that can be drawn through the furnace without overloading the gas cleaning equipment. Each smelting furnace operator can vary a number of parameters to increase production, but as the upper limit of production is approached, the likelihood of upsets that create environmental problems increase (see Section 3).

Temperature control is accomplished by adjusting the coke feed rate, blast air rate, or oxygen content of the blast air. Some smelters also have blast air preheat temperature controls. A relatively high ratio of coke (8 to 9 percent) is used in the charge to maximize production, and a relatively large operating temperature range can be achieved within the furnace by blast air control. Rapid smelting can thus be achieved by raising temperatures throughout the furnace with high blast air rates, preheat temperatures, and oxygen ratios.

The blast furnace operator may lose control of the furnace temperature. If the gases ignite, the fire cannot be extinguished simply by shutting off the blast air. In such cases, additional charge material without coke must usually be added to reduce the heat and extinguish the fire. Placing a steel cover on top can also help put out the fire.

Reverberatory Furnaces--

Reverberatory furnaces are typically rectangular and have an arched roof. The melt is directly exposed to the furnace burner flame. Figure 12 shows a

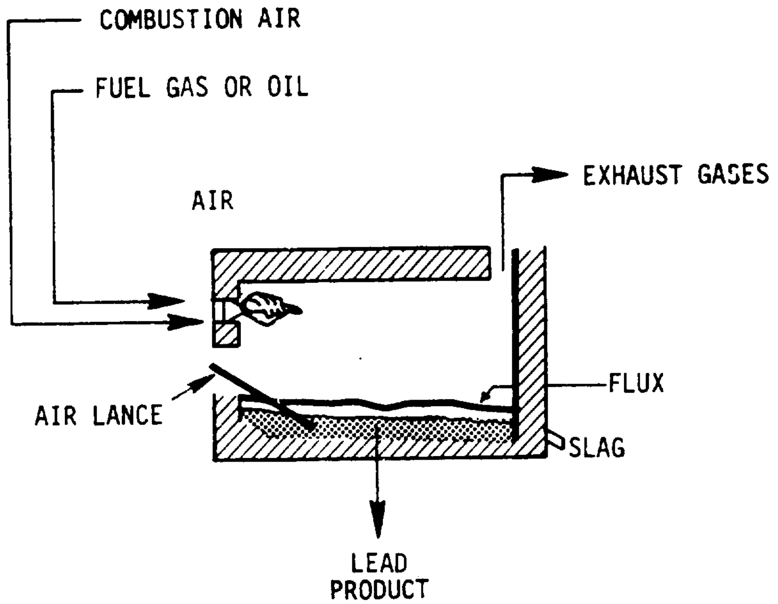


Figure 12. Schematic diagram of a reverberatory furnace.

schematic diagram of a reverberatory furnace. As discussed earlier, reverberatory furnaces are also used for sweating, melting, dust agglomeration, softening, and refining. Typically, a specific reverberatory furnace is used for only one of these functions. The processing steps vary, depending on the furnace function.

Battery plates, lead oxides, drosses from refining kettles, fluxes, and collected flue dusts are feed materials for reverberatory furnaces. Typical feed mechanisms are ram feeders and top charging doors with conveyors. Both feed mechanisms require manual attention. The high temperatures within reverberatory furnaces immediately vaporize any water that is introduced with the scrap. The consequent rapid increase in gas flow from the furnace can cause temporary overloading of the exhaust ventilation and process gas handling systems. Predrying of the raw material can prevent this problem.

Furnace temperatures vary with the operation and the type of fuel fired. Oil flames produce cooler, more radiant flames than natural gas. Although furnace exit gas temperatures may be as high as 1204°C (2200°F) in smelting applications, slag temperatures in the furnace rarely exceed 1010°C (1850°F), and metal temperature rarely exceed 955°C (1750°F).

(The slag floats on top of the melted lead and may be tapped from one or more locations around the furnace.) Access or inspection doors are usually provided at or just above the desired slag level. When the desired slag level is reached, the tap hole is opened and the slag drained from the furnace. A refractory launder (chute) is usually provided to allow the slag to flow into a receiving ladle. The receiving ladle should be allowed to cool under an exhaust hood until a crust forms on the slag. Ventilation should be provided for the slag hole, launder, and ladle to allow access during slag tapping. In some cases, reverberatory slags are too viscous to flow freely from the furnace. In such cases, the tapping operation requires the furnace operator to rake out the slag through a slag door having a launder attached to it. If slag tapping can be done at only one location in the furnace, it may be necessary to push the slag from several points around the furnace toward the slag tap door.

Crude lead may be tapped (as described in the discussion of blast furnaces) or pumped from the reverberatory furnace. This lead has less impurities than from the blast furnaces and is normally a soft lead. Often the lead is tapped into a holding kettle that is held at 427° to 538°C (800° to 1000°F). The crude lead is either cast into sows or hogs for later processing or can be pumped to refining and/or alloying kettles or to a casting operation for final processing.

A number of secondary lead smelters use reverberatory furnaces to produce soft or semisoft lead directly from battery plates and lead scrap. The furnace can be adjusted to oxidize all of the antimony in the scrap, but only part of the lead. A highly oxidized, antimonial slag is produced as a result. This slag is typically processed in either a rotary or a blast furnace to recover the metal values. The soft or semisoft lead can be sent to the refining or alloying kettle furnaces.

The recent increase in demand for soft lead for the manufacture of calcium-lead-tin (Ca-Pb-Sn) batteries has increased the need for reverberatory smelting and softening capacity. The decision to use a blast furnace/reverberatory furnace combination or only a reverberatory furnace is usually based on site-specific lead markets. Smelters who receive Ca-Pb-Sn batteries and battery manufacturing scrap and who supply manufacturers of Ca-Pb-Sn batteries may elect not to make antimonial lead.

Rotary Kiln Furnaces--

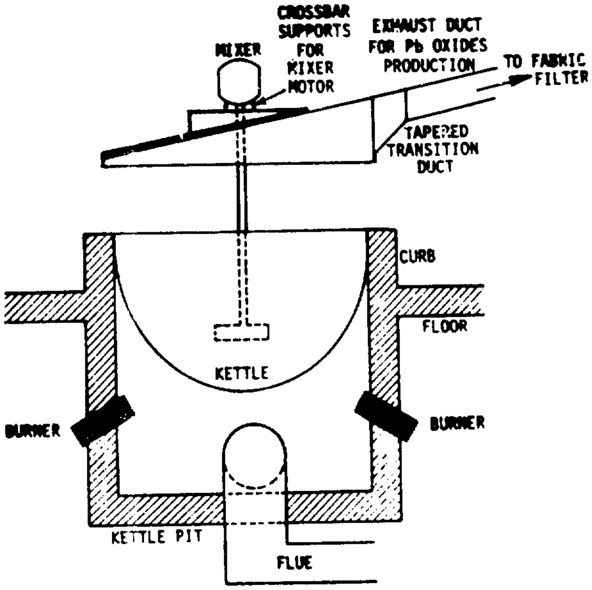
Rotary kiln furnaces are not used as widely as blast furnaces and reverberatory furnaces for smelting at secondary lead plants in the United States. One operating kiln is a 177 foot long, 10 foot diameter cement kiln that has been converted to lead smelting specifications (Egan 1980). The furnace is inclined slightly to the horozontal. Brick is used to form a dam around the perimeter of the discharge and to collect the metal.

Feed materials (lead bearing materials, fluxes, and coke) can be fed by a conveyor system into the higher end of the kiln. The feed is exposed to furnace temperatures of up to 1300°C (2400°F) generated mainly by the combustion of coke in the charge. A burner is located at the discharge end of the kiln to initiate the coke combustion as well as for slag temperature control. At the discharge end, the slag is floating on top of the hot metal and is continuously removed from the furnace by flowing over the brick dam. Lead is tapped periodically by stopping the kiln, breaking open the tap hole located behind the dam, and then rotating the kiln until the tap hole points down (Egan 1980). The lead produced by rotary kiln smelting is identical to that produced in reverberatory furnaces as discussed above.

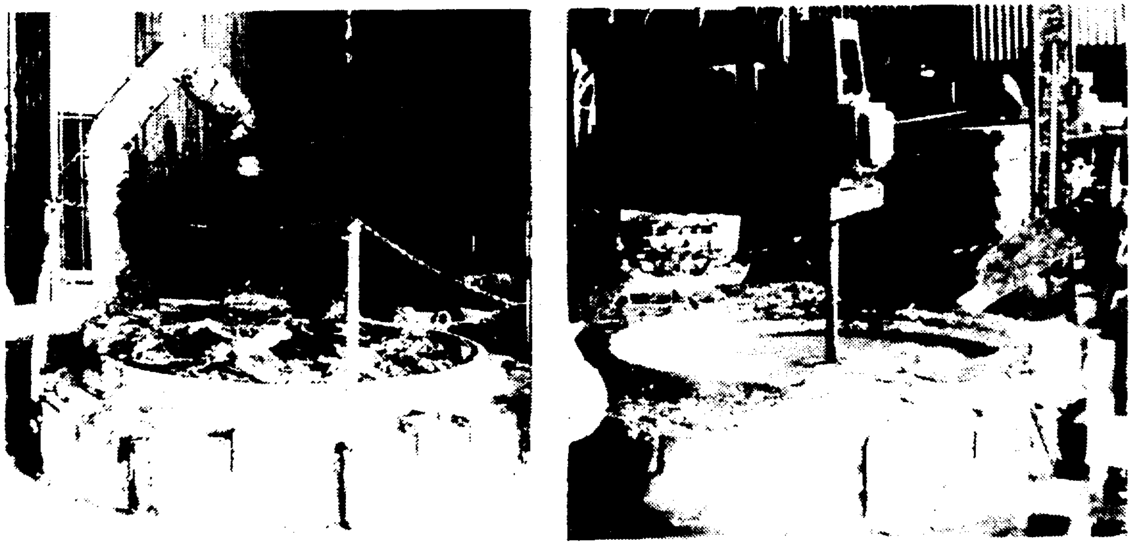
2.2.3 Refining (softening, alloying, and oxidation)

Refining and processing the crude lead from the smelting furnaces can consist of softening, alloying, and oxidation depending on the final products. Since intermediate smelting products, especially from blast furnaces, may contain antimony or copper (either element makes the lead hard), these contaminants must be removed to produce a soft lead product. Molten or cast lead bullion, fluxes (including sodium hydroxide, sodium nitrate, aluminum chloride, aluminum, sawdust, sulfur, and calcium chloride), and air may be inputs to this process. Sodium nitrate ($NaNO_3$), sodium hydroxide (NaOH), and air are used to reduce the antimony content of the charge. The addition of sodium nitrate and sodium hydroxide to the melt produces a slag/dross material that contains $NaSbO_3$. Aluminum reacts preferentially with copper, antimony, and nickel to form drosses that can be skimmed off the melt surface; sulfur is used to dross copper. Calcium chloride is used for detinning. Alloying processes involve adjustment of the metals content of smelting furnace lead to produce a desired lead alloy. Common alloying agents are antimony, copper, silver, and tin. Lead is oxidized to produce battery lead oxide (PbO containing approximatley 20 percent lead metal), and lead oxide pigments such as lead monoxide (PbO) and red lead (Pb_3O_4).

Kettle furnaces are generally used to refine and process lead because they allow better control of impurities and further alloying. Most kettles are heated by oil- or gas-fired burners located in brick-lined pits below the kettles as shown in Figure 13.



a. Kettle, pit, and exhaust system.



b. Melting operation for refining and alloying.

c. Kettle just before pouring.

Figure 13. Kettle furnace operations.

Kettles are used for softening processes to remove antimony and/or copper and thus produce a soft lead product. Kettle sizes generally range from 1 to 135 Mg (1 to 150 tons). The process steps are charging the preheated kettle, melting the charge, agitating the flux into the molten charge, skimming the drosses, and pouring or pumping the molten metal. In some cases, molten lead is charged directly from the smelting furnace into the refining kettle. Often, separate kettles are used to remove various impurities. Fluxing temperatures generally range between 375° and 485°C (700° and 900°F). Sometimes copper is precipitated by lowering the temperature to 325°C (620°F). Aluminum chloride or sawdust may be mixed into the dross to decrease the chemical bond between lead droplets and dross. The dross is skimmed or tapped from the furnace before the softened lead is tapped. The dross is usually reprocessed in a blast furnace to recover metal values.

The process steps for alloying are similar to those used for softening except that alloying agents are added to the melted lead and mixed into the charge before pouring and casting into pigs (Figure 14).

Oxidizing furnaces are either kettle or reverberatory furnaces which oxidize lead and entrain the product lead oxides in the combustion air stream. The product is subsequently recovered in baghouses at high efficiency. Battery lead oxide (PbO containing approximately 20 percent lead metal) is produced by kettle oxidation. The process steps are: charging the kettle by gravity with molten lead, agitating the molten lead with paddles, inducing a draft of air over the surface of the melt through a duct leading to a baghouse, and collecting the lead and lead oxide fumes in a baghouse. Lead oxide pigments, lead monoxide (PbO), and red lead (Pb_3O_4) are produced by reverberatory oxidation. The process steps are charging the preheated reverberatory furnace with molten lead, agitating and simultaneously oxidizing the molten lead, and removing the lead oxide form the furnace and cooling rapidly. Either lead monoxide (PbO) or red lead (Pb_3O_4) is produced by controlling the degree of oxidation.

2.2.4 Casting (Pigging)

The softened lead and lead alloy products are cast into pigs (ingots) with a pigging machine (Figure 14). The pigging machine is similar to a conveyor with molds forming the conveyor belt. Molds receive the liquid hot metal at one end of the machine, and by the time the mold is moved to the other end, the lead ingot (pig) is solidified. The pig is then dumped from the mold. The mold is then recycled to receive more hot metal.

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SECTION 3

AIR EMISSIONS GENERATION AND CONTROL

Furnace technology in the secondary lead industry has remained essentially unchanged for more than 50 years. Many furnace combinations are used, depending on the scrap supply and the desired product. Each furnace produces point source emissions and fugitive emissions. The lead content of particulate matter from each furnace varies with the furnace feed material, furnace temperature, and oxidation potential of the furnace gas. Figure 15 indicates the major sources of environmental emissions from secondary lead processes.

Table 1 lists sources of fugitive emissions from secondary lead smelters. Fugitive emission rates vary with each operation. When the furnaces are open (e.g., during charging) fugitive emission rates are highest. At other times, fugitive emission rates can be essentially nil. Smelting furnaces account for a significant portion of both process and fugitive emissions, but vehicular traffic, flue dust handling, and cleanup operations can create additional fugitive emissions problems that are independent of furnace operating conditions. In some older smelters, the accumulation of dust settled on the ground over the years has created a continual reentrainment problem arising from windblown dust that results in ambient lead levels exceeding 1.5 $\mu g/m^3$ off the smelter property, even after the facility has been shut down. The Section 3 References (Page 49) lists important sources for data on emissions from secondary lead smelting operations.

Major changes in secondary lead smelters have been the addition of emission control systems and control methods for process and ventilation gases. Acceptable control practices can be divided into process controls, process emission controls, and fugitive emission controls. Control practices are further classified as engineering controls and procedural controls. Engineering controls include the following:

Isolation of process or employee

Enclosure of process or employee

Ventilation (either local exhaust and capture or dilution)

Substitution of materials, processes, equipment, or operating practices

Physical modification of contaminants (e.g., wetting the material)

Reduction or elimination of emission producing energy to the source (e.g., not overheating molten metal or not sweeping dry, dusty materials)

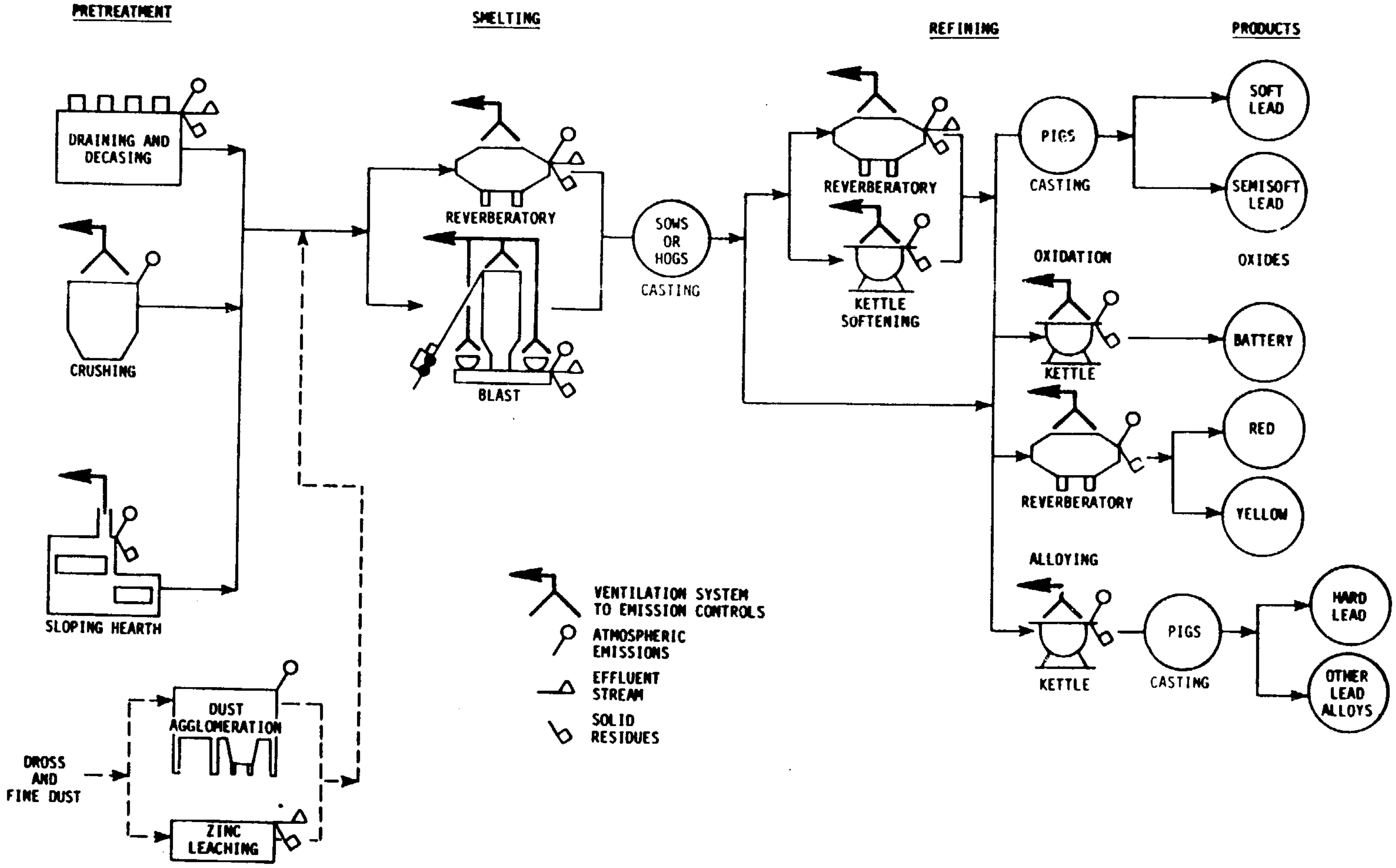

Figure 15. Sources of air emissions from secondary lead plants.

TABLE 1. SOURCES AND EMISSION FACTORS FOR POINT AND FUGITIVE EMISSIONS FROM SECONDARY LEAD SMELTERS[a,b]

Source	Point source emissions, lb/ton			Fugitive emissions, lb/ton		
	Particulate	Lead	Basis[c]	Particulate	Lead	Basis[c]
Raw material handling and transfer (scrap lead, scrap iron, coke, limestone, etc.)	NA	NA		NA	NA	
Lead and iron scrap burning	NA	NA		NA	NA	
Battery decasing	NA	NA		NA	NA	
Crushing or shredding	NA	NA		NA	NA	
Rotary or reverberatory furnace sweating	32-70	7-16	E			
Charging				1.6-3.5	0.4-1.8	E
Tapping						
Scrap removal						
Reverberatory furnace smelting	147	34	B			
Charging				2.8-15.7	0.6-3.6	E
Slag tapping						
Lead tapping/casting						
Blast furnace smelting	193	44	B			
Charging						
Slag tapping						
Lead tapping/casting						
Holding pot	NA	NA		NA	NA	
Reverberatory furnace softening	NA	NA		NA	NA	
Charging						
Tapping (drossing, skimming, lead removal)						
Kettle softening/refining	0.8	0.2	B	0.04	0.01	E
Charging						
Tapping (drossing, skimming, lead removal)						
Kettle alloying/refining						
Charging						
Tapping, drossing, skimming						
Kettle oxidation[d]	<40	NA	E	NA	NA	
Charging						
Reverberatory furnace oxidation	NA	NA		NA	NA	
Charging						
Casting (pigging)[e]	NA	NA		0.88	0.2	E
Flue dust handling and transfer	NA	NA		NA	NA	
Vehicular traffic	NA	NA		NA	NA	
Traffic on paved roads						
Traffic on unpaved roads						
Hooding, ductwork, control device, or furnace leaks	NA	NA		NA	NA	

NA - data not available.

[a] Source: Reference 9.

[b] All emission factors are based on the quantity of material charged to the furnace (except particulate kettle oxidation).

[c] The basis of the emission factor refers to the method from which the emission factor was obtained.
B - Emission factor based on source test data and is rated (EPA 1980) as above average.
E - Engineering estimate supportable by visual observation and emission tests for similar sources. These emission factors are rated (EPA 1980) poor.

[d] Factors based on amount of lead oxide produced.

[e] Factors based on amount of lead cast.

Use of applicable control devices (e.g., central vacuum systems or electrostatic foggers)

Procedural controls include the following:

Operating practice instructions

Employee work practices, job descriptions, and incentives

Housekeeping practices and policies

Maintenance practices and policies

This section describes both point and fugitive process emission sources and their associated control alternatives.

3.1 PROCESS EMISSIONS

Air emissions are generated at all secondary lead plant operations. Raw material handling and preparation, smelting, and refining processes are sources of point as well as fugitive emissions. In addition to lead, antimony, nickel, tin, and zinc, arsenic is also a pollutant of concern. Arsenic is found in varying amounts in lead scrap. It is contained in primary lead unless removed in refining, and it is often added during lead alloying as a hardening agent. Antimonial lead (hard lead) is used primarily in the posts and grids of lead-acid storage batteries and for lead cable sheathing (PEDCo 1982). The arsenic in such alloys ranges from 0.15 percent for antimonial lead to no more than 0.5 percent for arsenical lead (Burgess 1976).

3.1.1 Raw Material Handling and Pretreatment

Raw Material Handling and Transport--
Lead bearing feed materials are commonly stored outdoors in large piles (Figure 16) and are transported around the smelter in front-end loaders and/or trucks. If these materials are allowed to dry, wind erosion becomes a major source of fugitive emissions. Indoor storage is possible and would significantly reduce the fugitive emissions but the high cost of large structures has discouraged many facilities from using this technique. There are no estimates available for fugitive emissions from raw material handling and transport operations.

Battery Handling--
Battery handling and breaking consists of the following operations: segregation by the type of battery case material; battery sawing or crushing; acid draining; and lead scrap removal. Emissions consist mainly of sulfuric acid mist and dusts containing dirt, battery case material and lead compounds. There are no available emission factor estimates from battery handling operations.

Figure 16. Unagglomerated baghouse dust.

Sweating--

Sweating furnaces operate with gas exit temperatures of 538° to 816°C (1000° to 1500°F) from both reverberatory and rotary sweating furnaces. Atmospheric emissions consist of fume, dust, soot, particulates, and combustion products, including sulfur dioxide (SO_2). The SO_2 emissions are from the combustion of sulfur compounds from both the scrap and the fuel. Particulate emissions from the stack range from 16 to 35 kg/Mg (32-70 lb/ton) of material feed with dust loadings of 3.2 to 10.3 g/m^3 (1.4-4.5 gr/ft^3)(EPA 1980). Lead emissions are estimated to be 4 to 8 kg/Mg (7-16 lb/ton) (EPA 1980). Fugitive emissions are generated during charging and removing the scrap from the furnace. Estimated fugitive emissions from sweating furnaces are 0.8 to 1.8 kg/Mg (1.6-3.5 lb/ton) for particulates and 0.2 to 0.4 kg/Mg (0.4-1.8 lb/ton) for lead (EPA 1980).

Reverberatory furnaces for sweating require the removal of solid scrap parts after the lead or solder has been melted away. Hoes or rakes are used to remove the scrap through access doors. This operation can create fugitive emissions and drag dust from the furnace hearth.

Dust Agglomeration--

Dust agglomeration is not performed at all plants. It is frequently used to minimize fugitive emissions when recycling fabric filter dusts from reverberatory, blast, and rotary furnaces. There are no readily available emission estimates for dust agglomeration furnaces.

3.1.2 Smelting

Blast Furnace--

The process gas temperature at the exit from American blast furnaces normally range from 121° to 425°C (250° to 800°F). This temperature strongly influences the quantity and composition of material in the process gases from individual furnaces (Schwitzgebel 1981). Blast furnace emissions include carbon monoxide (CO), sulfur dioxide (SO_2), sulfuric acid (H_2SO_4), and particulate matter that contains lead, antimony, chlorine, sulfur, and organic materials. Table 2 shows lead distribution in blast and reverberatory furnace dust.

TABLE 2. LEAD DISTRIBUTION IN REVERBERATORY AND BLAST FURNACE SMELTING (Burton 1980)
(%)

	Lead in raw material charge	Lead in slag	Lead in fumes and dusts
Reverberatory furnace smelting	47	46	7
Blast furnace smelting	70	8	12

A Canadian study of fabric filter and flue dusts from 10 sources shows that the lead content in the sources ranged from 15.8 to 68.7 percent with an average of 51.7 percent (McDonnell and Hilborn 1978). Another source indicated that the lead blast furnace flue dust is 80 to 90 percent metal and that 70 to 80 percent of the metal is lead (i.e., that the flue dust is 56 to 72 percent lead).* Point source emissions from blast furnace operation are estimated to average 97 kg/Mg (193 lb/ton) of material charged for particulate, 22 kg/Mg (44 lb/ton) for lead, and 27 kg/Mg (53 lb/ton) for SO_2 (EPA 1980).

Fugitive emissions from the blast furnace result from the following operations:

Furnace charging
Tuyere punching
Slag tapping
Crude lead tapping
Process upsets

Emission estimates are not available for each of these operations, but total fugitive emissions from smelting operations are estimated to be 1.4 to 7.9 kg/Mg (2.8-15.7 lb/ton) of charge material for particulate and 0.3 to 1.8 kg/Mg (0.6-3.6 lb/ton) for lead (EPA 1980).

Front-end loaders are potential fugitive emissions sources during the charging operation, as are the skip hoist, conveyors, and furnace charging area itself. Skip hoists and conveyors in this application are likely to collect dust and battery residue that may be subsequently dispersed into the air when the machine is impacted or vibrated vigorously.

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* Personal communication with F. Ledbetter, U.S. EPA, Region IV, December 18, 1979.

Routine tending of a blast furnace involves examination of each tuyere either by removing the tuyere cover or by viewing it through a transparent window in the cover (Figure 17). When the tuyere cover is removed for

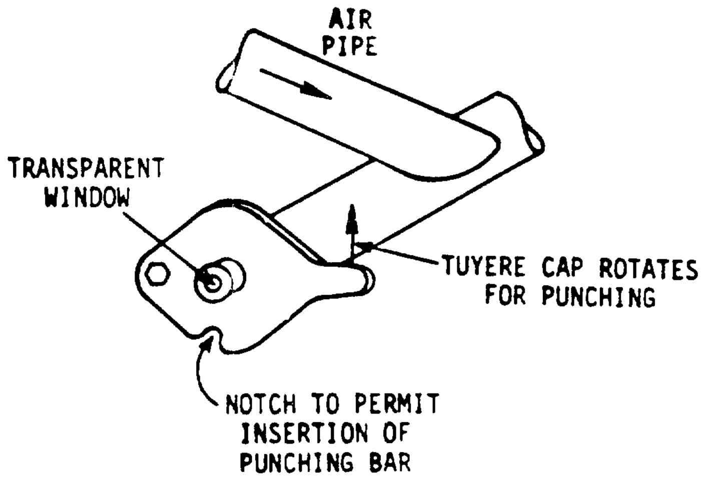

Figure 17. Tuyere cap.

inspection of the slag level or for punching, some emissions occur. The transparent window in the tuyere cover minimizes the necessity to remove the cover and hence reduces emissions.

Slag is tapped from holes bored through the furnace refractory between the lead well surface and the tuyere level. One to four tap holes may be used, depending on the size and shape of the furnace. This process is labor intensive and can be a source of fugitive emissions from the time the holes are tapped until they are sealed with fire-clay plugs. The slag tapping operation is repeated every 15 to 20 minutes, depending on the rate of operation and the material being smelted.

Crude lead tapping is another source of fugitive emissions from the blast furnace. These emissions occur as the crude lead is being continuously tapped from a tap hole below the slag level (Figure 18).

Fugitive emissions can also occur if the production limitation of the furnace is exceeded. Furnace capacity is usually limited by the gas handling capacity of the control equipment attached to the furnace. If the gas handling capacity is exceeded, excess emissions occur through leaks in the system; e.g., leaks from the furnace top, flanges, inspection covers, or doors. Even if local exhaust ventilation is provided for such fugitive emissions, fires and explosions can occur because these fugitive emissions bypass the afterburner and are ducted to the sanitary baghouse. At the high end of the temperature range, (e.g., 425°C gas exit temperature) fires in the scrap charge are a danger. Thus, control of the temperature profile within the furnace has an important effect on furnace emissions.

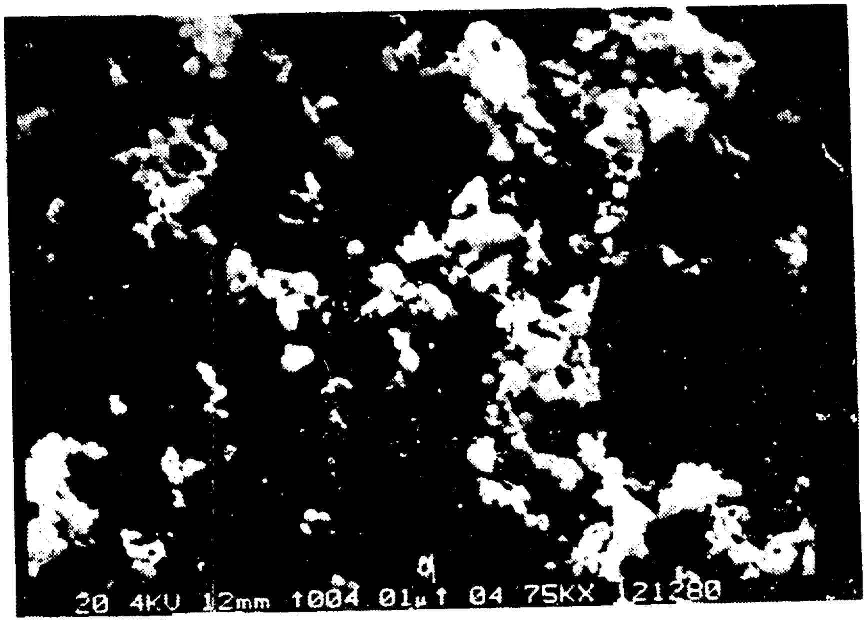

Figure 18. Electron micrograph of lead well dust. Magnification - 4750 X.

Reverberatory Furnaces--

Reverberatory furnace off-gas temperatures range from 538° to 1315°C (1000° to 2400°F), depending on the function of the furnace, the operation being performed, the firing rate, and the feed material. The furnace gases are usually well oxidized. In most furnaces, excess combustion air is supplied to ensure that adequate combustion occurs at the burner end of the furnace, where smelting occurs. The furnaces are also operated at a very slightly negative pressure, typically between -2.48 and -24.8 Pa (-0.01 and -0.1 in. H_2O). This causes a slight flow of air into the furnace that helps to complete the combustion of hot gases and particulate matter.

Reverberatory emissions can be expected to be similar to those from blast furnace smelting if battery scrap is the furnace feed material. Reverberatory furnaces that are charged with crude lead instead of scrap will not emit chlorine or sulfur compounds; those compounds were already removed in the production of the crude lead.

Emissions from reverberatory furnaces used for smelting have been estimated to be an average of 74 kg/Mg (147 lb/ton) of material charged for particulate, 17 kg/Mg (34 lb/ton) for lead, and 40 kg/Mg (80 lb/ton) for SO_2 (EPA 1980). Off gas temperatures range from 530° to 1315°C (1000° to 2400°F).

Fugitive emissions result from the following operations:

- Furnace charging
- Slag tapping
- Crude lead tapping
- Cooler (hairpin) cleaning (where applicable)

or alloying kettle furnaces.

No specific fugitive emission data were available for reverberatory smelting. One estimate, however, for fugitive emissions from smelting is 1.4 to 7.9 kg/Mg (2.8-15.7 lb/ton) of feed material for particulate, and 0.3 to 1.8 kg/Mg (0.6-3.6 lb/ton) for lead (EPA 1980).

Furnace charging is a significant source of fugitive emissions. Ram feeders and top charging doors with conveyors are typical feeding mechanisms for reverberatory furnaces. Both feed mechanisms require manual attention. Although exhaust ventilation and partial enclosure is possible, the high temperatures within reverberatory furnaces immediately vaporize any water that is introduced with the scrap. The consequent rapid increase in gas flow from the furnace can cause temporary overloading of the exhaust ventilation and process gas handling systems. Fugitive dust is emitted from access doors and charge ports, and through the furnace refractory. Leaks through the refractory are probably the most difficult fugitive emission problem to solve with reverberatory furnaces.

Fugitive emissions can escape during slag tapping. Slag may be tapped from one or more locations around the furnace. Access or inspection doors are usually provided at or just above the desired slag level. Fugitive emissions escape when the doors are opened. When the desired slag level is reached, the tap hole is opened and the slag drained from the furnace.

In some cases, reverberatory slags are dusty. They are often too viscous to flow freely from the furnace. In such cases, the tapping operation requires the furnace operator to rake out the slag through a slag door having a launder attached to it. If slag tapping can be done at only one location in the furnace, it may be necessary to push the slag from several points around the furnace toward the slag tap door. When access doors for pushing the slag are open, the potential for fugitive emissions is great, especially if moist charge materials are being fed to the furnace.

During crude lead tapping, fugitive emissions will escape from the launder and receiving kettle, ladle, or casting operation during the metal taps.

Reverberatory gases may be cooled in hairpin type coolers (Figure 19) or by dilution with process or ventilation gases prior to particulate collection. The long continuous run of ductwork which makes up a hairpin cooler appears as several verticle rows of hairpins. The gases are cooled in hairpin coolers because of the heat loss from the large surface area of the ductwork. Some particulate matter collects at the base of the hairpin coolers and must be periodically removed. Unless this collected material is conveyed automatically in an enclosed system, it can create a fugitive emission problem.

3.1.3 Refining (Softening, Alloying, and Oxidation)

Process gases, fumes, and dusts are emitted from kettle furnaces used for refining processes. Combustion gases are often vented directly to the atmosphere without being mixed with the process gases. Emissions from softening and alloying are estimated to be 0.4 kg/Mg (0.8 lb/ton) of material charged for particulate, and 0.1 kg/Mg (0.2 lb/ton) for lead (EPA 1980). The upper limit for lead oxide escaping from product collection for kettle oxidaton is 20 kg/Mg (40 lb/ton) of lead oxide produced for particulate (EPA 1980).

kettles as shown in Figure 13.

① Fug. emissions occur ~~when~~ during the molten lead transfer when the hood is opened to insert the pump.

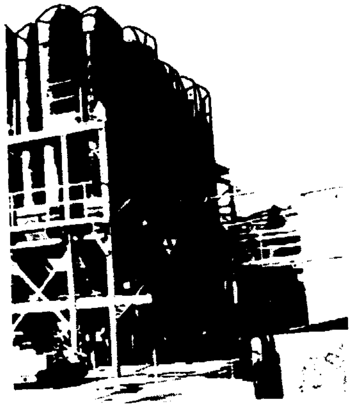

Figure 19. Hairpin cooler.

Lead refining and the production of lead, tin, and antimonial alloys pose potential fugitive emission problems because of the employees' continued contact with the process. Charging, melting, fluxing, mixing, drossing, skimming, and tapping operations require the operator to open kettle hood doors and to partially disrupt local exhaust ventilation. Lead dust and fume, agitated molten metal, high temperatures, and a number of chemical agents all contribute to the potential for fugitive emissions. Total fugitives from kettle refining are estimated to be 0.02 kg/Mg (0.04 lb/ton) of material charged for particulate and 0.004 kg/Mg (0.01 lb/ton) for lead (EPA 1980).

Little charge preparation is required for kettles. Fugitive emissions may result from melting the residual lead inside the lead pumps (i.e., the lead in the pumps solidifies between uses and heating is necessary to melt the contained lead so that the pump impeller is freed) so that the pumps can be used. This can best be done by immersing the pump in the kettle, since the pumps are relatively portable and thus, lead fumes are captured by the kettle hood.

Fugitive emissions occur during fluxing, mixing, and drossing, and skimming operations through openings required to complete these operations. The proper use of the hood doors during these operations can minimize openings as well as fugitive emissions. The higher metal temperatures, additional agitation, and presence of dusty dross materials create a greater fugitive dust potential.

Antimonial drosses are a major fugitive problem with kettle furnaces. These dusty materials are usually skimmed manually from the lead surface with hoes, rakes, or shovels. During the drossing operation, kettle temperatures are typically above 343°C (650°F), kettle doors are at least partially open, and ~~the~~ normal flow pattern of the local exhaust ventilation is disturbed.

① Casting; fugitive emissions occur - the casting operation. 0.44 kg/Mg (.88 lb/ton) of particulate & 0.1 kg/Mg (0.2 lb/ton) for lead