12.11 Secondary Lead Processing

12.11.1 General

Secondary lead smelters produce lead and lead alloys from lead-bearing scrap material. More than 60 percent of all secondary lead is derived from scrap automobile batteries. Each battery contains approximately 8.2 kg (18 lb) of lead, consisting of 40 percent lead alloys and 60 percent lead oxide. Other raw materials used in secondary lead smelting include wheel balance weights, pipe, solder, drosses, and lead sheathing. Lead produced by secondary smelting accounts for half of the lead produced in the U. S. There are 42 companies operating 50 plants with individual capacities ranging from 907 megagrams (Mg) (1,000 tons) to 109,000 Mg (120,000 tons) per year.

12.11.2 Process Description[1-7]

Secondary lead smelting includes 3 major operations: scrap pretreatment, smelting, and refining. These are shown schematically in Figure 12.11-1A, Figure 12.11-1B, and Figure 12.11-1C, respectively.

12.11.2.1 Scrap Pretreatment -

Scrap pretreatment is the partial removal of metal and nonmetal contaminants from lead-bearing scrap and residue. Processes used for scrap pretreatment include battery breaking, crushing, and sweating. Battery breaking is the draining and crushing of batteries, followed by manual separation of the lead from nonmetallic materials. Lead plates, posts, and intercell connectors are collected and stored in a pile for subsequent charging to the furnace. Oversized pieces of scrap and residues are usually put through jaw crushers. This separated lead scrap is then sweated in a gas- or oil-fired reverberatory or rotary furnace to separate lead from metals with higher melting points. Rotary furnaces are usually used to process low-lead-content scrap and residue, while reverberatory furnaces are used to process high-lead-content scrap. The partially purified lead is periodically tapped from these furnaces for further processing in smelting furnaces or pot furnaces.

12.11.2.2 Smelting -

Smelting produces lead by melting and separating the lead from metal and nonmetallic contaminants and by reducing oxides to elemental lead. Smelting is carried out in blast, reverberatory, and rotary kiln furnaces. Blast furnaces produce hard or antimonial lead containing about 10 percent antimony. Reverberatory and rotary kiln furnaces are used to produce semisoft lead containing 3 to 4 percent antimony; however, rotary kiln furnaces are rarely used in the U. S. and will not be discussed in detail.

In blast furnaces pretreated scrap metal, rerun slag, scrap iron, coke, recycled dross, flue dust, and limestone are used as charge materials to the furnace. The process heat needed to melt the lead is produced by the reaction of the charged coke with blast air that is blown into the furnace. Some of the coke combusts to melt the charge, while the remainder reduces lead oxides to elemental lead. The furnace is charged with combustion air at 3.4 to 5.2 kPa (0.5 to 0.75 psi) with an exhaust temperature ranging from 650 to 730°C (1200 to 1350°F).

As the lead charge melts, limestone and iron float to the top of the molten bath and form a flux that retards oxidation of the product lead. The molten lead flows from the furnace into a holding pot at a nearly continuous rate. The product lead constitutes roughly 70 percent of the charge. From

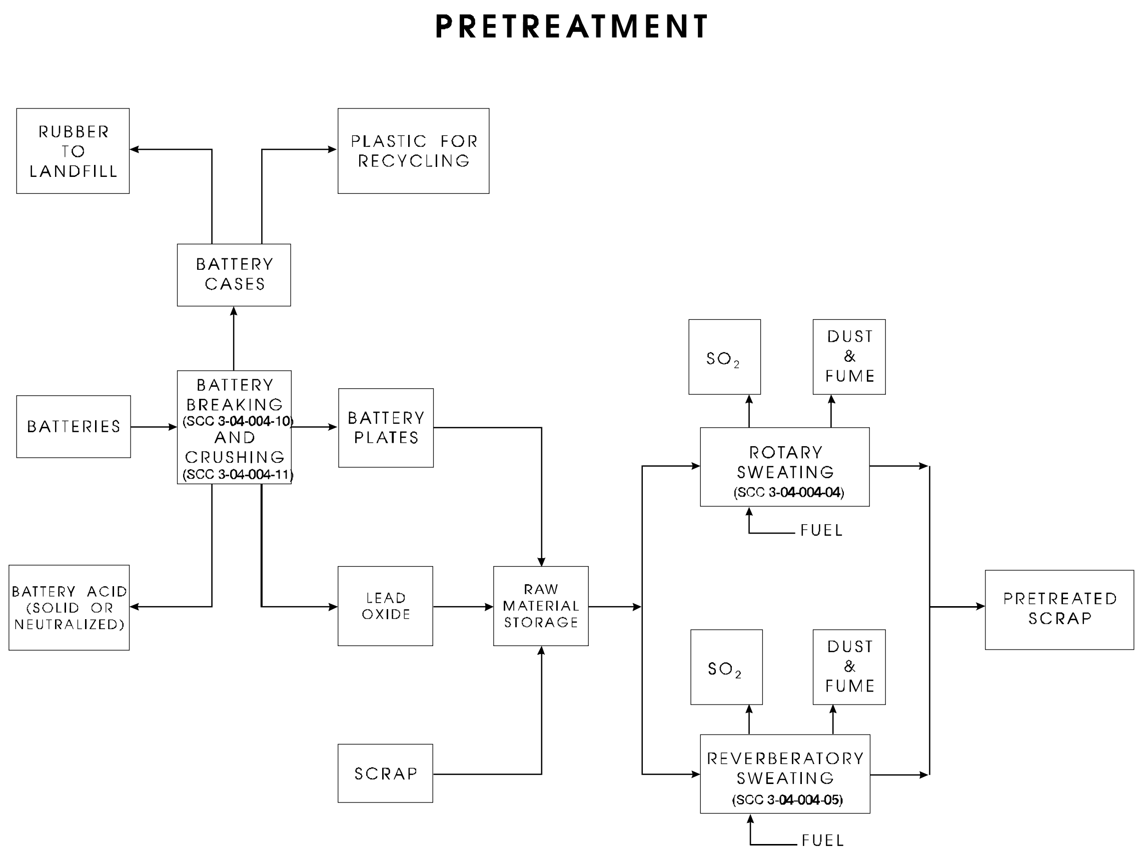

Figure 12.11-1A. Process flow for typical secondary lead smelting.
(Source Classification Codes in parentheses.)

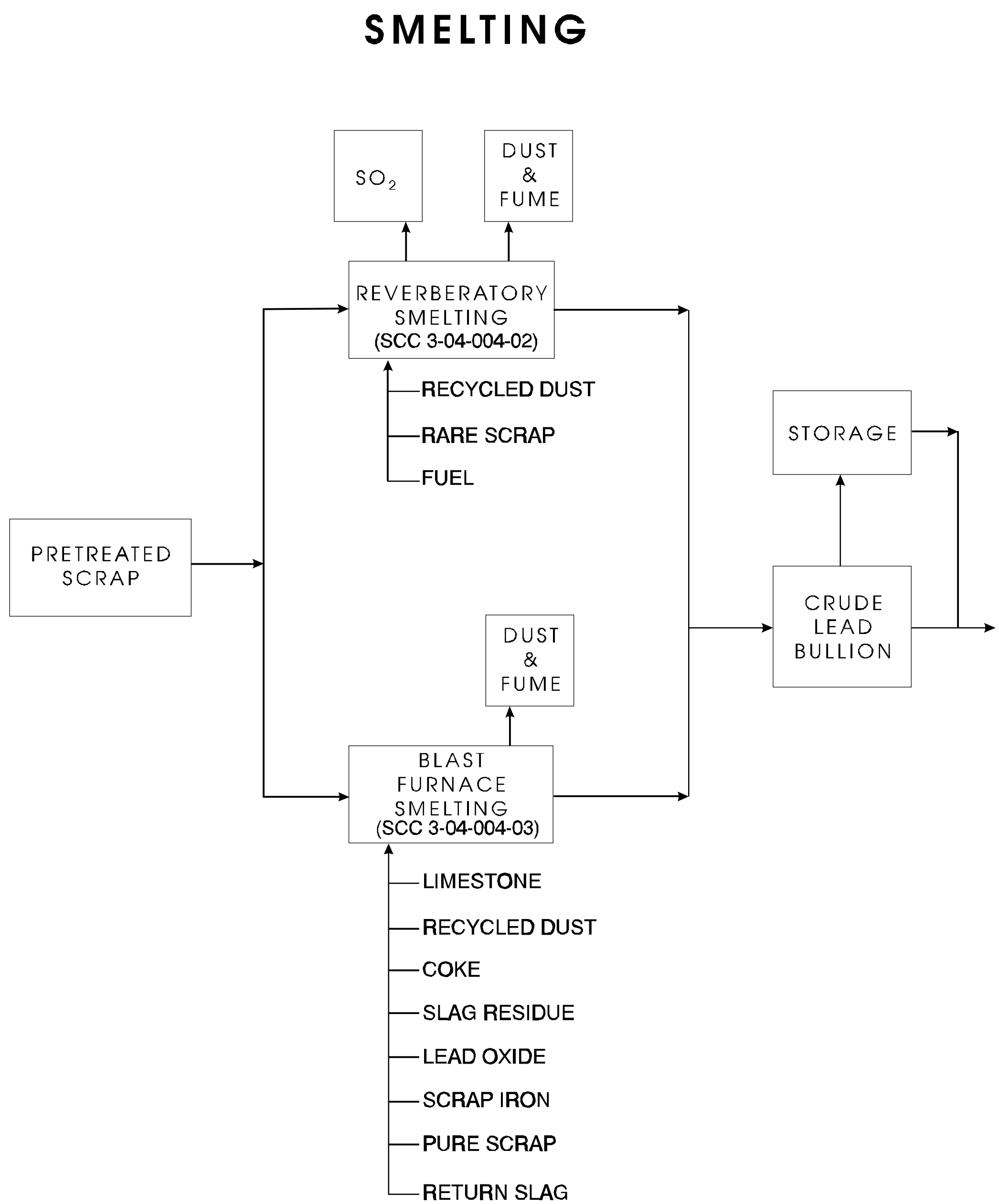

Figure 12.11-1B. Process flow for typical secondary lead smelting. (Source Classification Codes in parentheses.)

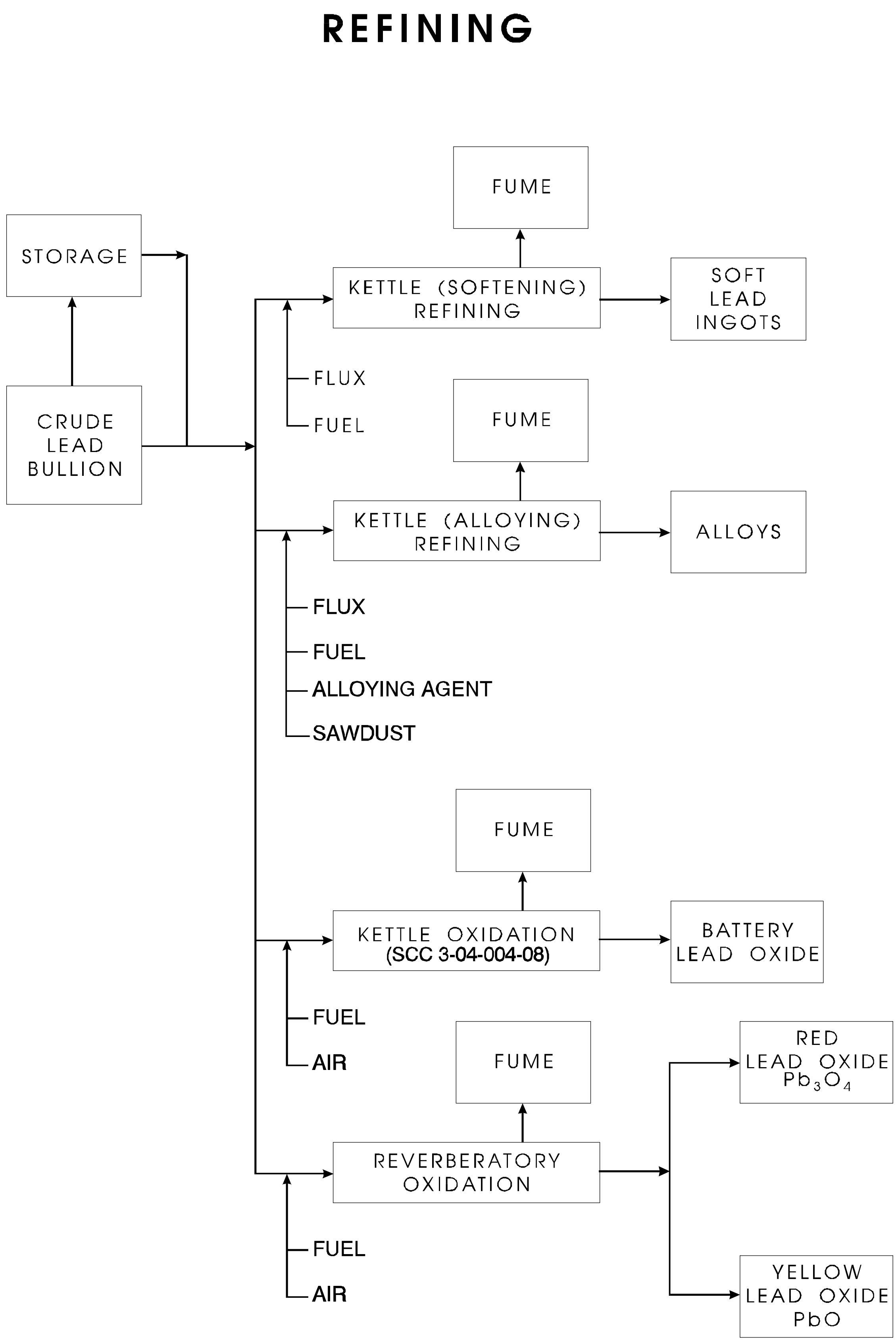

Figure 12.11-1C. Process flow for typical secondary lead smelting.
(Source Classification Codes in parentheses.)

the holding pot, the lead is usually cast into large ingots called pigs or sows. About 18 percent of the charge is recovered as slag, with about 60 percent of this being a sulfurous slag called matte. Roughly 5 percent of the charge is retained for reuse, and the remaining 7 percent of the charge escapes as dust or fume. Processing capacity of the blast furnace ranges from 18 to 73 Mg per day (20 to 80 tons per day).

The reverberatory furnace used to produce semisoft lead is charged with lead scrap, metallic battery parts, oxides, drosses, and other residues. The charge is heated directly to a temperature of 1260°C (2300°F) using natural gas, oil, or coal. The average furnace capacity is about 45 megagrams (50 tons) per day. About 47 percent of the charge is recovered as lead product and is periodically tapped into molds or holding pots. Forty-six percent of the charge is removed as slag and is later processed in blast furnaces. The remaining 7 percent of the furnace charge escapes as dust or fume.

12.11.2.3 Refining -

Refining and casting the crude lead from the smelting furnaces can consist of softening, alloying, and oxidation depending on the degree of purity or alloy type desired. These operations are batch processes requiring from 2 hours to 3 days. These operations can be performed in reverberatory furnaces; however, kettle-type furnaces are most commonly used. Remelting process is usually applied to lead alloy ingots that require no further processing before casting. Kettle furnaces used for alloying, refining, and oxidizing are usually gas- or oil-fired, and have typical capacities of 23 to 136 megagrams (25 to 150 tons) per day. Refining and alloying operating temperatures range from 320 to 700°C (600 to 1300°F). Alloying furnaces simply melt and mix ingots of lead and alloy materials. Antimony, tin, arsenic, copper, and nickel are the most common alloying materials.

Refining furnaces are used to either remove copper and antimony for soft lead production, or to remove arsenic, copper, and nickel for hard lead production. Sulfur may be added to the molten lead bath to remove copper. Copper sulfide skimmed off as dross may subsequently be processed in a blast furnace to recover residual lead. Aluminum chloride flux may be used to remove copper, antimony, and nickel. The antimony content can be reduced to about 0.02 percent by bubbling air through the molten lead. Residual antimony can be removed by adding sodium nitrate and sodium hydroxide to the bath and skimming off the resulting dross. Dry drossing consists of adding sawdust to the agitated mass of molten metal. The sawdust supplies carbon to help separate globules of lead suspended in the dross and to reduce some of the lead oxide to elemental lead.

Oxidizing furnaces, either kettle or reverberatory units, are used to oxidize lead and to entrain the product lead oxides in the combustion air stream for subsequent recovery in high-efficiency baghouses.

12.11.3 Emissions And Controls[1,4-5]

Emission factors for controlled and uncontrolled processes and fugitive particulate are given in Tables 12.11-1, 12.11-2, 12.11-3, and 12.11-4. Particulate emissions from most processes are based on accumulated test data, whereas fugitive particulate emissions are based on the assumption that 5 percent of uncontrolled stack emissions are released as fugitive emissions.

Reverberatory and blast furnaces account for the vast majority of the total lead emissions from the secondary lead industry. The relative quantities emitted from these 2 smelting processes cannot be specified, because of a lack of complete information. Most of the remaining processes are small emission sources with undefined emission characteristics.

Table 12.11-1 (Metric Units). EMISSION FACTORS FOR SECONDARY LEAD PROCESSING[a]

Process	Particulate[b]				Lead[b]				SO_2	
	Uncontrolled	EMISSION FACTOR RATING	Controlled	EMISSION FACTOR RATING	Uncontrolled	EMISSION FACTOR RATING	Controlled	EMISSION FACTOR RATING	Uncontrolled	EMISSION FACTOR RATING
Sweating[c] (kg/Mg charge) (SCC 3-04-004-04)	16-35	E	ND	NA	4-8[d]	E	ND	NA	ND	ND
Reverberatory smelting (SCC 3-04-004-02)	162 (87-242)[e]	C	0.50 (0.26-0.77)[f]	C	32 (17-48)[g]	C	ND	NA	40 (36-44)[f]	C
Blast smelting-cupola[h] (SCC 3-04-004-03)	153 (92-207)[j]	C	1.12 (0.11-2.49)[k]	C	52 (31-70)[m]	C	0.15 (0.02-0.32)[n]	C	27 (9-55)[e]	C
Kettle refining (SCC 3-04-004-26)	0.02[p]	C	ND	NA	0.006[p]	C	ND	NA	ND	NA
Kettle Oxidation (SCC 3-04-004-08)	≤ 20[q]	E	ND	NA	ND	NA	ND	NA	ND	NA
Casting (SCC 3-04-004-09)	0.02[p]	C	ND	NA	0.007[p]	C	ND	NA	ND	NA

[a] Emission factor units expressed as kg of pollutant/Mg metal produced. SCC = Source Classification Code. ND = no data. NA = not applicable.
[b] Particulate and lead emission factors are based on quantity of lead product produced, except as noted.
[c] Reference 1. Estimated from sweating furnace emissions from nonlead secondary nonferrous processing industries.
[d] References 3,5. Based on assumption that uncontrolled reverberatory furnace flue emissions are 23% lead.
[e] References 8-11.
[f] References 6,8-11.
[g] Reference 13. Uncontrolled reverberatory furnace flue emissions assumed to be 23% lead. Blast furnace emissions have lead content of 34%, based on single uncontrolled plant test.
[h] Blast furnace emissions are combined flue gases and associated ventilation hood streams (charging and tapping).
[j] References 8,11-12.
[k] References 6,8,11-12,14-15.
[m] Reference 13. Blast furnace emissions have lead content of 26%, based on single controlled plant test.
[n] Based on quantity of material charged to furnaces.
[p] Reference 13. Lead content of kettle refining emissions is 40% and of casting emissions is 36%.
[q] References 1-2. Essentially all product lead oxide is entrained in an air stream and subsequently recovered by baghouse with average collection efficiency >99%. Factor represents emissions of lead oxide that escape a baghouse used to collect the lead oxide product. Represents approximate upper limit for emissions.

Table 12.11-2 (English Units). EMISSION FACTORS FOR SECONDARY LEAD PROCESSING[a]

Process	Particulate[b]				Lead[b]				SO_2	
	Uncontrolled	EMISSION FACTOR RATING	Controlled	EMISSION FACTOR RATING	Uncontrolled	EMISSION FACTOR RATING	Controlled	EMISSION FACTOR RATING	Uncontrolled	EMISSION FACTOR RATING
Sweating[c] (kg/Mg charge) (SCC 3-04-004-04)	32-70	E	ND	NA	7-16[d]	E	ND	NA	ND	NA
Reverberatory smelting (SCC 3-04-004-02)	323 (173-483)[e]	C	1.01 (0.53-1.55)[f]	C	65 (35-97)[g]	C	ND	NA	80 (71-88)[f]	C
Blast smelting-cupola[h] (SCC 3-04-004-03)	307 (184-413)[j]	C	2.24 (0.22-4.88)[k]	C	104 (64-140)[m]	C	0.29 (0.03-0.64)[n]	C	53 (18-110)[e]	C
Kettle refining (SCC 3-04-004-26)	0.03[p]	C	ND	NA	0.01[p]	C	ND	NA	ND	NA
Kettle Oxidation (SCC 3-04-004-08)	≤ 40[p]	E	ND	NA	ND	NA	ND	NA	ND	NA
Casting (SCC 3-04-004-09)	0.04[p]	C	ND	NA	0.01[p]	C	ND	NA	ND	NA

[a] Emission factors expressed as lb of pollutant/ton of metal produced. SCC = Source Classification Code. ND = no data. NA = not applicable.
[b] Particulate and lead emission factors are based on quantity of lead product produced, except as noted.
[c] Reference 1. Estimated from sweating furnace emissions from nonlead secondary nonferrous processing industries.
[d] References 3,5. Based on assumption that uncontrolled reverberatory furnace flue emissions are 23% lead.
[e] References 8-11.
[f] References 6,8-11.
[g] Reference 13. Uncontrolled reverberatory furnace flue emissions assumed to be 23% lead. Blast furnace emissions have lead content of 34%, based on single uncontrolled plant test.
[h] Blast furnace emissions are combined flue gases and associated ventilation hood streams (charging and tapping).
[j] References 8,11-12.
[k] References 6,8,11-12,14-15.
[m] Reference 13. Blast furnace emissions have lead content of 26%, based on single controlled plant test.
[n] Based on quantity of material charged to furnaces.
[p] Reference 13. Lead content of kettle refining emissions is 40% and of casting emissions is 36%.
[q] References 1-2. Essentially all product lead oxide is entrained in an air stream and subsequently recovered by baghouse with average collection efficiency >99%. Factor represents emissions of lead oxide that escape a baghouse used to collect the lead oxide product. Represents approximate upper limit for emissions.

Table 12.11-3 (Metric Units). FUGITIVE EMISSION FACTORS FOR SECONDARY LEAD PROCESSING[a]

EMISSION FACTOR RATING: E

Operation	Particulate	Lead
Sweating (SCC 3-04-004-12)	0.8-1.8[b]	0.2-0.9[c]
Smelting (SCC 3-04-004-13)	4.3-12.1	0.1-0.3[d]
Kettle refining (SCC 3-04-004-14)	0.001	0.0003[e]
Casting (SCC 3-04-004-25)	0.001	0.0004[e]

[a] Reference 16. Based on amount of lead product except for sweating, which is based on quantity of material charged to furnace. Fugitive emissions estimated to be 5% of uncontrolled stack emissions. SCC= Source Classification Code.
[b] Reference 1. Sweating furnace emissions estimated from nonlead secondary nonferrous processsing industries.
[c] References 3,5. Assumes 23% lead content of uncontrolled blast furnace flue emissions.
[d] Reference 24.
[e] Reference 13.

Table 12.11-4 (English Units). FUGITIVE EMISSION FACTORS FOR SECONDARY LEAD PROCESSING[a]

EMISSION FACTOR RATING: E

Operation	Particulate	Lead
Sweating (SCC 3-04-004-12)	1.6-3.5[b]	0.4-1.8[c]
Smelting (SCC 3-04-004-13)	8.6-24.2	0.2-0.6[d]
Kettle refining (SCC 3-04-004-14)	0.002	0.0006[e]
Casting (SCC 3-04-004-25)	0.002	0.0007[e]

[a] Reference 16. Based on amount of lead product, except for sweating, which is based on quantity of material charged to furnace. Fugitive emissions estimated to be 5% of uncontrolled stack emissions. SCC = Source Classification Code.
[b] Reference 1. Sweating furnace emissions estimated from nonlead secondary nonferrous processsing industries.
[c] References 3,5. Assumes 23% lead content of uncontrolled blast furnace flue emissions.
[d] Reference 24.
[e] Reference 13.

Emissions from battery breaking are mainly of sulfuric acid mist and dusts containing dirt, battery case material, and lead compounds. Emissions from crushing are also mainly dusts.

Emissions from sweating operations are fume, dust, soot particles, and combustion products, including sulfur dioxide (SO_2). The SO_2 emissions come from combustion of sulfur compounds in the scrap and fuel. Dust particles range in size from 5 to 20 micrometers (µm) and unagglomerated lead fumes range in size from 0.07 to 0.4 µm, with an average diameter of 0.3 µm. Particulate loadings in the stack gas from reverberatory sweating range from 3.2 to 10.3 grams per cubic meter (1.4 to 4.5 grains per cubic foot). Baghouses are usually used to control sweating emissions, with removal efficiencies exceeding 99 percent. The emission factors for lead sweating in Tables 12.11-1 and 12.11-2 are based on measurements at similar sweating furnaces in other secondary metal processing industries, not on measurements at lead sweating furnaces.

Reverberatory smelting furnaces emit particulate and oxides of sulfur and nitrogen. Particulate consists of oxides, sulfides and sulfates of lead, antimony, arsenic, copper, and tin, as well as unagglomerated lead fume. Particulate loadings range from to 16 to 50 grams per cubic meter (7 to 22 grains per cubic foot). Emissions are generally controlled with settling and cooling chambers, followed by a baghouse. Control efficiencies generally exceed 99 percent. Wet scrubbers are sometimes used to reduce SO_2 emissions. However, because of the small particles emitted from reverberatory furnaces, baghouses are more often used than scrubbers for particulate control.

Two chemical analyses by electron spectroscopy have shown the particulate to consist of 38 to 42 percent lead, 20 to 30 percent tin, and about 1 percent zinc.[17] Particulate emissions from reverberatory smelting furnaces are estimated to contain 20 percent lead.

Emissions from blast furnaces occur at charging doors, the slag tap, the lead well, and the furnace stack. The emissions are combustion gases (including carbon monoxide, hydrocarbons, and oxides of sulfur and nitrogen) and particulate. Emissions from the charging doors and the slag tap are hooded and routed to the devices treating the furnace stack emissions. Blast furnace particulate is smaller than that emitted from reverberatory furnaces and is suitable for control by scrubbers or fabric filters downstream of coolers. Efficiencies for various control devices are shown in Table 12.11-5. In one application, fabric filters alone captured over 99 percent of the blast furnace particulate emissions.

Particulate recovered from the uncontrolled flue emissions at 6 blast furnaces had an average lead content of 23 percent.[3,5] Particulate recovered from the uncontrolled charging and tapping hoods at 1 blast furnace had an average lead content of 61 percent.[13] Based on relative emission rates, lead is 34 percent of uncontrolled blast furnace emissions. Controlled emissions from the same blast furnace had lead content of 26 percent, with 33 percent from flues, and 22 percent from charging and tapping operations.[13] Particulate recovered from another blast furnace contained 80 to 85 percent lead sulfate and lead chloride, 4 percent tin, 1 percent cadmium, 1 percent zinc, 0.5 percent antimony, 0.5 percent arsenic, and less than 1 percent organic matter.[18]

Kettle furnaces for melting, refining, and alloying are relatively minor emission sources. The kettles are hooded, with fumes and dusts typically vented to baghouses and recovered at efficiencies exceeding 99 percent. Twenty measurements of the uncontrolled particulates from kettle furnaces showed a mass median aerodynamic particle diameter of 18.9 micrometers, with particle size ranging from 0.05 to 150 micrometers. Three chemical analyses by electron spectroscopy showed the composition of particulate to vary from 12 to 17 percent lead, 5 to 17 percent tin, and 0.9 to 5.7 percent zinc.[16]

Table 12.11-5. EFFICIENCIES OF PARTICULATE CONTROL EQUIPMENT ASSOCIATED WITH SECONDARY LEAD SMELTING FURNACES

Control Equipment	Furnace Type	Control Efficiency (%)
Fabric filter[a]	Blast Blast Reverberatory	98.4 99.2
Dry cyclone plus fabric filter[a]	Blast	99.0
Wet cyclone plus fabric filter[b]	Reverberatory	99.7
Settling chamber plus dry cyclone plus fabric filter[c]	Reverberatory	99.8
Venturi scrubber plus demister[d]	Blast	99.3

[a] Reference 8.
[b] Reference 9.
[c] Reference 10.
[d] Reference 14.

Emissions from oxidizing furnaces are economically recovered with baghouses. The particulates are mostly lead oxide, but they also contain amounts of lead and other metals. The oxides range in size from 0.2 to 0.5 µm. Controlled emissions have been estimated to be 0.1 kilograms per megagram (0.2 pounds per ton) of lead product, based on a 99 percent efficient baghouse.

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