12.1 Primary Aluminum Production

12.1.1 General[1]

Primary aluminum refers to aluminum produced directly from mined ore. The ore is refined and electrolytically reduced to elemental aluminum. There are 13 companies operating 23 primary aluminum reduction facilities in the U. S. In 1991, these facilities produced 4.5 million tons of primary aluminum.

12.1.2 Process Description[2-3]

Primary aluminum production begins with the mining of bauxite ore, a hydrated oxide of aluminum consisting of 30 to 56 percent alumina (Al_2O_3) and lesser amounts of iron, silicon, and titanium. The ore is refined into alumina by the Bayer process. The alumina is then shipped to a primary aluminum plant for electrolytic reduction to aluminum. The refining and reducing processes are seldom accomplished at the same facility. A schematic diagram of primary aluminum production is shown in Figure 12.1-1.

12.1.2.1 Bayer Process Description -

In the Bayer process, crude bauxite ore is dried, ground in ball mills, and mixed with a preheated spent leaching solution of sodium hydroxide (NaOH). Lime (CaO) is added to control phosphorus content and to improve the solubility of alumina. The resulting slurry is combined with sodium hydroxide and pumped into a pressurized digester operated at 221 to 554°F. After approximately 5 hours, the slurry of sodium aluminate ($NaAl_2OH$) solution and insoluble red mud is cooled to 212°F and sent through either a gravity separator or a wet cyclone to remove coarse sand particles. A flocculent, such as starch, is added to increase the settling rate of the red mud. The overflow from the settling tank contains the alumina in solution, which is further clarified by filtration and then cooled. As the solution cools, it becomes supersaturated with sodium aluminate. Fine crystals of alumina trihydrate ($Al_2O_3 \cdot 3H_2O$) are seeded in the solution, causing the alumina to precipitate out as alumina trihydrate. After being washed and filtered, the alumina trihydrate is calcined to produce a crystalline form of alumina, which is advantageous for electrolysis.

12.1.2.2 Hall-Heroult Process -

Crystalline Al_2O_3 is used in the Hall-Heroult process to produce aluminum metal. Electrolytic reduction of alumina occurs in shallow rectangular cells, or "pots", which are steel shells lined with carbon. Carbon electrodes extending into the pot serve as the anodes, and the carbon lining serves as the cathode. Molten cryolite (Na_3AlF_6) functions as both the electrolyte and the solvent for the alumina. The electrolytic reduction of Al_2O_3 by the carbon from the electrode occurs as follows:

$$2Al_2O_3 + 3C \rightarrow 4Al + 3CO_2 \qquad (1)$$

Aluminum is deposited at the cathode, where it remains as molten metal below the surface of the cryolite bath. The carbon anodes are continuously depleted by the reaction. The aluminum product is tapped every 24 to 48 hours beneath the cryolite cover, using a vacuum siphon. The aluminum is then transferred to a reverberatory holding furnace where it is alloyed, fluxed, and

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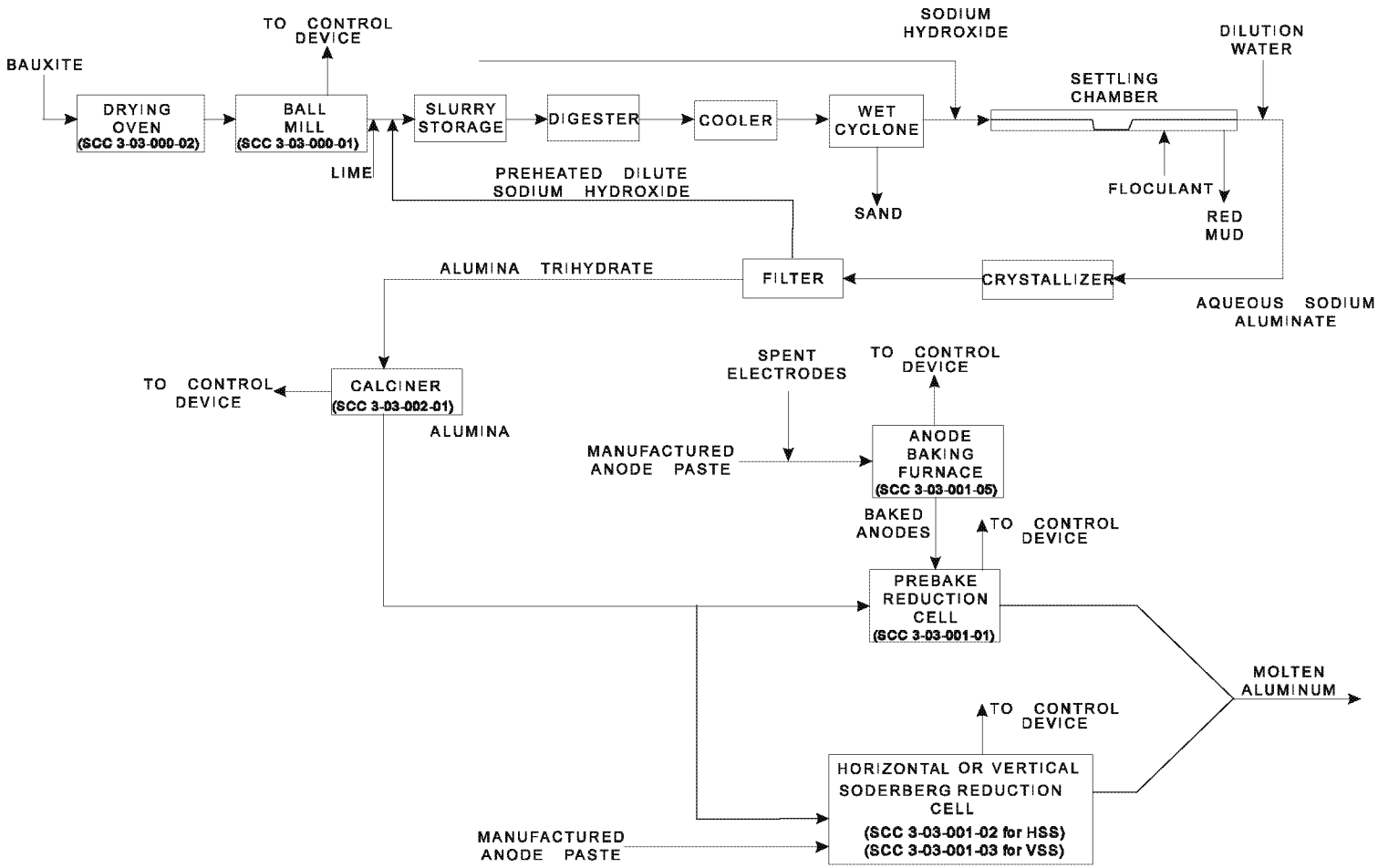

Figure 12.1-1. Schematic diagram of aluminum production process. (Source Classification Codes in parentheses.)

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degassed to remove trace impurities. (Aluminum reverberatory furnace operations are discussed in detail in Section 12.8, "Secondary Aluminum Operations".) From the holding furnace, the aluminum is cast or transported to fabricating plants.

Three types of aluminum reduction cells are now in use: prebaked anode cell (PB), horizontal stud Soderberg anode cell (HSS), and vertical stud Soderberg anode cell (VSS). Most of the aluminum produced in the U. S. is processed using the prebaked cells.

All three aluminum cell configurations require a "paste" (petroleum coke mixed with a pitch binder). Paste preparation includes crushing, grinding, and screening of coke and blending with a pitch binder in a steam jacketed mixer. For Soderberg anodes, the thick paste mixture is added directly to the anode casings. In contrast, the prebaked ("green") anodes are produced as an ancillary operation at a reduction plant.

In prebake anode preparation, the paste mixture is molded into green anode blocks ("butts") that are baked in either a direct-fired ring furnace or a Reid Hammer furnace, which is indirectly heated. After baking, steel rods are inserted and sealed with molten iron. These rods become the electrical connections to the prebaked carbon anode. Prebaked cells are preferred over Soderberg cells because they are electrically more efficient and emit fewer organic compounds.

12.1.3 Emissions And Controls[2-10]

Controlled and uncontrolled emission factors for total particulate matter, gaseous fluoride, and particulate fluoride are given in Table 12.1-1. Table 12.1-2 gives available data for size-specific particulate matter emissions for primary aluminum industry processes.

In bauxite grinding, hydrated aluminum oxide calcining, and materials handling operations, various dry dust collection devices (centrifugal collectors, multiple cyclones, or Electrostatic precipitators (ESPs) and/or wet scrubbers) have been used. Large amounts of particulate are generated during the calcining of hydrated aluminum oxide, but the economic value of this dust leads to the use of extensive controls which reduce emissions to relatively small quantities.

Emissions from aluminum reduction processes are primarily gaseous hydrogen fluoride and particulate fluorides, alumina, carbon monoxide, carbon dioxide (CO_2), volatile organics, and sulfur dioxide (SO_2) from the reduction cells. The source of fluoride emissions from reduction cells is the fluoride electrolyte, which contains cryolite, aluminum fluoride (AlF_3), and fluorospar (CaF_2). The dissociation of the molten cryolite is the source of the perfluorinated carbons (PFCs) — tetrafluoromethane (CF_4) and hexafluoroethane (C_2F_6) — which are formed during anode effects. The factors related to the formation of PFCs are not currently well understood, but they can be formed either by direct reaction of the fluorine with the carbon anode or electrochemically.[11] The emission factors for CF_4 and C_2F_6 presented here should be used with caution due to the lack of information on their formation. Table 12.1-3 presents emission factors for greenhouse gases. The CO_2 emission factors shown in Table 12.1-3 assume that all of the carbon used in the production process is emitted as CO_2. While some of the carbon is emitted as CO, there is insufficient data to develop emission factors for CO. Therefore, the carbon emitted as CO is treated here as CO_2 because it is assumed that it will eventually be oxidized to CO_2 after being emitted. Because the primary source of carbon in the anodes is petroleum coke (some is also from the pitch binder), care must be taken not to double count CO_2 emissions in a greenhouse gas emissions inventory if the CO_2 emissions from aluminum production are also accounted for as a non-fuel use of petroleum coke.

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Particulate emissions from reduction cells include alumina and carbon from anode dusting, and cryolite, aluminum fluoride, calcium fluoride, chiolite ($Na_5Al_3F_{14}$), and ferric oxide. Representative size distributions for fugitive emissions from PB and HSS plants, and for particulate emissions from HSS cells, are presented in Table 12.1-2.

Emissions from reduction cells also include hydrocarbons or organics, carbon monoxide, and sulfur oxides. These emission factors are not presented here because of a lack of data. Small amounts of hydrocarbons are released by PB pots, and larger amounts are emitted from HSS and VSS pots. In vertical cells, these organics are incinerated in integral gas burners. Sulfur oxides originate from sulfur in the anode coke and pitch, and concentrations of sulfur oxides in VSS cell emissions range from 200 to 300 parts per million. Emissions from PB plants usually have SO_2 concentrations ranging from 20 to 30 parts per million.

Emissions from anode bake ovens include the products of fuel combustion; high boiling organics from the cracking, distillation, and oxidation of paste binder pitch; sulfur dioxide from the sulfur in carbon paste, primarily from the petroleum coke; fluorides from recycled anode butts; and other particulate matter. Emission factors for these components are not included in this document due to insufficient data. Concentrations of uncontrolled SO_2 emissions from anode baking furnaces range from 5 to 47 parts per million (based on 3 percent sulfur in coke).

High molecular weight organics and other emissions from the anode paste are released from HSS and VSS cells. These emissions can be ducted to gas burners to be oxidized, or they can be collected and recycled or sold. If the heavy tars are not properly collected, they can cause plugging of exhaust ducts, fans, and emission control equipment.

A variety of control devices has been used to abate emissions from reduction cells and anode baking furnaces. To control gaseous and particulate fluorides and particulate emissions, 1 or more types of wet scrubbers (spray tower and chambers, quench towers, floating beds, packed beds, venturis) have been applied to all 3 types of reduction cells and to anode baking furnaces. In addition, particulate control methods such as wet and dry electrostatic precipitators (ESPs), multiple cyclones, and dry alumina scrubbers (fluid bed, injected, and coated filter types) are used on all 3 cell types and with anode baking furnaces.

The fluoride adsorption system is becoming more prevalent and is used on all 3 cell types. This system uses a fluidized bed of alumina, which has a high affinity for fluoride, to capture gaseous and particulate fluorides. The pot offgases are passed through the crystalline form of alumina, which was generated using the Bayer process. A fabric filter is operated downstream from the fluidized bed to capture the alumina dust entrained in the exhaust gases passing through the fluidized bed. Both the alumina used in the fluidized bed and that captured by the fabric filter are used as feedstock for the reduction cells, thus effectively recycling the fluorides. This system has an overall control efficiency of 99 percent for both gaseous and particulate fluorides. Wet ESPs approach adsorption in particulate removal efficiency, but they must be coupled to a wet scrubber or coated baghouse to catch hydrogen fluoride.

Scrubber systems also remove a portion of the SO_2 emissions. These emissions could be reduced by wet scrubbing or by reducing the quantity of sulfur in the anode coke and pitch (i.e., calcining the coke).

The molten aluminum may be batch treated in furnaces to remove oxide, gaseous impurities, and active metals such as sodium and magnesium. One process consists of adding a flux of chloride and fluoride salts and then bubbling chlorine gas, usually mixed with an inert gas, through the molten mixture. Chlorine

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The molten aluminum may be batch treated in furnaces to remove oxide, gaseous impurities, and active metals such as sodium and magnesium. One process consists of adding a flux of chloride and fluoride salts and then bubbling chlorine gas, usually mixed with an inert gas, through the molten mixture. Chlorine reacts with the impurities to form HCl, Al_2O_3, and metal chloride emissions. A dross forms on the molten aluminum and is removed before casting.

Potential sources of fugitive particulate emissions in the primary aluminum industry are bauxite grinding, materials handling, anode baking, and the 3 types of reduction cells (see Table 12.1-1). These fugitive emissions probably have particulate size distributions similar to those presented in Table 12.1-2.

12.1.4 Changes to Section Since 10/86

- Reformatted in 1995 for the 5th Edition.
- For Supplement D to the 5th Edition, the tables with metric units were removed and some text and emission factors were added for the Greenhouse gases (CO_2, CF_4, and C_2F_6).

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- Editorial corrections were made. In Table 12.1-2, the total cumulative emissions factor for Prebake Aluminum Cells was corrected from 2.5 to 5.0 lb/ton.
- Notes D and E were added to the table to clarify emissions factors and size distributions.
- Source classification codes were added to Table 12.1-3.

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Table 12.1-1. EMISSION FACTORS FOR PRIMARY ALUMINUM PRODUCTION PROCESSES (lb/ton Al produced)[a]
EMISSION FACTOR RATING: A

Operation	Total Particulate[b]	Gaseous Fluoride	Particulate Fluoride	Reference
Bauxite grinding[c] (SCC 3-03-000-01)				
Uncontrolled	6.0	Neg	Neg	1,3
Spray tower	1.8	Neg	Neg	1,3
Floating bed scrubber	1.7	Neg	Neg	1,3
Quench tower and spray screen	1.0	Neg	Neg	1,3
Aluminum hydroxide calcining[d] (SCC 3-03-002-01)				
Uncontrolled[e]	200.0	Neg	Neg	1,3
Spray tower	60.0	Neg	Neg	1,3
Floating bed scrubber	56.0	Neg	Neg	1,3
Quench tower	34.0	Neg	Neg	1,3
ESP	4.0	Neg	Neg	1,3
Anode baking furnace (SCC 3-03-001-05)				
Uncontrolled	3.0	0.9	0.1	2,12-13
Fugitive (SCC 3-03-001-11)	ND	ND	ND	NA
Spray tower	0.75	0.04	0.03	12
ESP	0.75	0.04	0.03	2
Dry alumina scrubber	0.06	0.009	0.002	2,12
Prebake cell (SCC 3-03-001-01)				
Uncontrolled	94.0	24.0	20.0	1-2,12-13
Fugitive (SCC 3-03-001-08)	5.0	1.2	1.0	2,12
Emissions to collector	89.0	22.8	19.0	2
Multiple cyclones	19.6	22.8	4.2	2
Dry alumina scrubber	1.8	0.2	0.4	2,12
Dry ESP plus spray tower	4.5	1.4	3.4	2,12
Spray tower	112.8	1.4	3.8	2
Floating bed scrubber	112.8	0.5	3.8	2
Coated bag filter dry scrubber	1.8	3.4	0.4	2
Crossflow packed bed	26.3	6.7	5.6	12
Dry plus secondary scrubber	0.7	0.4	0.3	12

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Table 12.1-1 (Cont.)

Operation	Total Particulate[b]	Gaseous Fluoride	Particulate Fluoride	Reference
Vertical Soderberg stud cell (SCC 3-03-001-03)				
Uncontrolled	78.0	33.0	11.0	2,12
Fugitive (SCC 3-03-001-10)	12.0	4.9	1.7	12
Emissions to collector	66.0	28.1	9.3	12
Spray tower	16.5	0.3	2.3	2
Venturi scrubber	2.6	0.3	0.4	2
Multiple cyclones	33.0	28.1	4.7	2
Dry alumina scrubber	1.3	0.3	0.2	2
Scrubber plus ESP plus spray screen and scrubber	7.7	1.5	1.3	2
Horizontal Soderberg stud cell (SCC 3-03-001-02)				
Uncontrolled	98.0	22.0	12.0	2,12
Fugitive (SCC 3-03-001-09)	10.0	2.2	1.2	2,12
Emissions to collector	88.0	19.8	10.8	2,12
Spray tower	22.0	7.5	2.7	2,12
Floating bed scrubber	19.4	0.4	2.4	2
Scrubber plus wet ESP	1.8	0.2	0.2	2,12
Wet ESP	1.8	1.0	0.2	12
Dry alumina scrubber	1.8	0.4	0.2	12

[a] To convert from lb/ton to kg/Mg, multiply by 0.5. SCC = Source Classification Code. Neg = negligible. ND = no data. NA = not applicable. Sulfur oxides may be estimated, with an EMISSION FACTOR RATING of C, by the following calculations.

Anode baking furnace, uncontrolled SO_2 emissions (excluding furnace fuel combustion emissions):

$$40(C)(S)(1-0.01\ K)\ \text{lb/ton}$$

Prebake (reduction) cell, uncontrolled SO_2 emissions:

$$0.4(C)(S)(K)\ \text{lb/ton}$$

where:

C = Anode consumption* during electrolysis, lb anode consumed/lb Al produced

S = % sulfur in anode before baking

K = % of total SO_2 emitted by prebake (reduction) cells.

*Anode consumption weight is weight of anode paste (coke + pitch) before baking.

[b] Includes particulate fluorides, but does not include condensible organic particulate.

[c] For bauxite grinding, units are lb of pollutant/ton of bauxite processed.

[d] For aluminum hydroxide calcining, units are lb of pollutant/ton of alumina produced.

[e] After multicyclones.

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Table 12.1-2. UNCONTROLLED EMISSION FACTORS AND PARTICLE SIZE DISTRIBUTION IN ALUMINUM PRODUCTION[a]

EMISSION FACTOR RATING: D (except as noted)

	Prebake Aluminum Cells[cd]		HSS Aluminum Cells[d]		HSS Reduction Cells[e]	
Particle Size[b] (μm)	Cumulative Mass % ≤ Stated Size	Cumulative Emission Factor (lb/ton Al produced)	Cumulative Mass % ≤ Stated Size	Cumulative Emission Factor (lb/ton Al produced)	Cumulative Mass % ≤ Stated Size	Cumulative Emission Factor (lb/ton Al produced)
0.625	13	0.67	8	0.8	26	25.5
1.25	18	0.92	13	1.3	32	31.4
2.5	28	1.40	17	1.7	40	39.2
5	43	2.15	23	2.3	50	49.0
10	58	2.90	31	3.1	58	56.8
15	65	3.23	39	3.9	63	61.7
Total	100	5.0[f]	100	10.0	100	98

[a] Reference 5. To convert from lb/ton to kg/Mg, multiply by 0.5.
[b] Expressed as equivalent aerodynamic particle diameter.
[c] EMISSION FACTOR RATING: C
[d] Emissions factors and size distributions are fugitive emissions measured from the roof monitor.
[e] Emissions factors and size distributions are for primary emissions.
[f] Emission factor was corrected 4/07. Editorial correction.

Table 12.1-3. GREENHOUSE GAS EMISSION FACTORS FOR PRIMARY ALUMINUM PRODUCTION PROCESSES[a]

Source Category	Pollutant	Emission Factor (lb/ton Al produced)	EMISSION FACTOR RATING	Notes
Aluminum Production — Soderberg Process[b] (SCC 3-03-001-02 and 3-03-001-03)[c]	CO_2	3670	C	Assumes carbon consumption of 0.50 lb C/lb Al produced.
Aluminum Production — Prebake Process[b] (SCC 3-03-001-01)	CO_2	3080	C	Assumes carbon consumption of 0.42 lb C/lb Al produced.
Aluminum Production (SCC 3-03-001-01, 3-03-001-02, 3-03-001-03)[c]	CF_4	1.2	E	Industry average. Varies with duration of anode effect, frequency, and current efficiency.
Aluminum Production (SCC 3-03-001-01, 3-03-001-02, 3-03-001-03)[c]	C_2F_6	0.12	E	Industry average. Varies with duration of anode effect, frequency, and current efficiency.

[a] References 11,14-17. To convert from lb/ton to kg/Mg, multiply by 0.5.
[b] Double counting of emissions will occur if CO_2 emissions from aluminum production are also accounted for as a non-fuel use of petroleum coke in a greenhouse gas inventory.
[c] Source Classification Codes were added to the table 4/07.

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