

12.1 Primary Aluminum Production

12.1.1 General¹

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 4.1 million megagrams (Mg) (4.5 million tons) of primary aluminum.

12.1.2 Process Description²⁻³

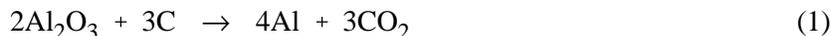
Primary aluminum production begins with the mining of bauxite ore, a hydrated oxide of aluminum consisting of 30 to 56 percent alumina (Al_2O_3) and lesser amounts of iron, silicon, and titanium. The ore is refined into alumina by the Bayer process. The alumina is then shipped to a primary aluminum plant 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 105 to 290°C (221 to 554°F). After approximately 5 hours, the slurry of sodium aluminate (NaAl_2OH) solution and insoluble red mud is cooled to 100°C (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 ($\text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$) 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 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:



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 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.

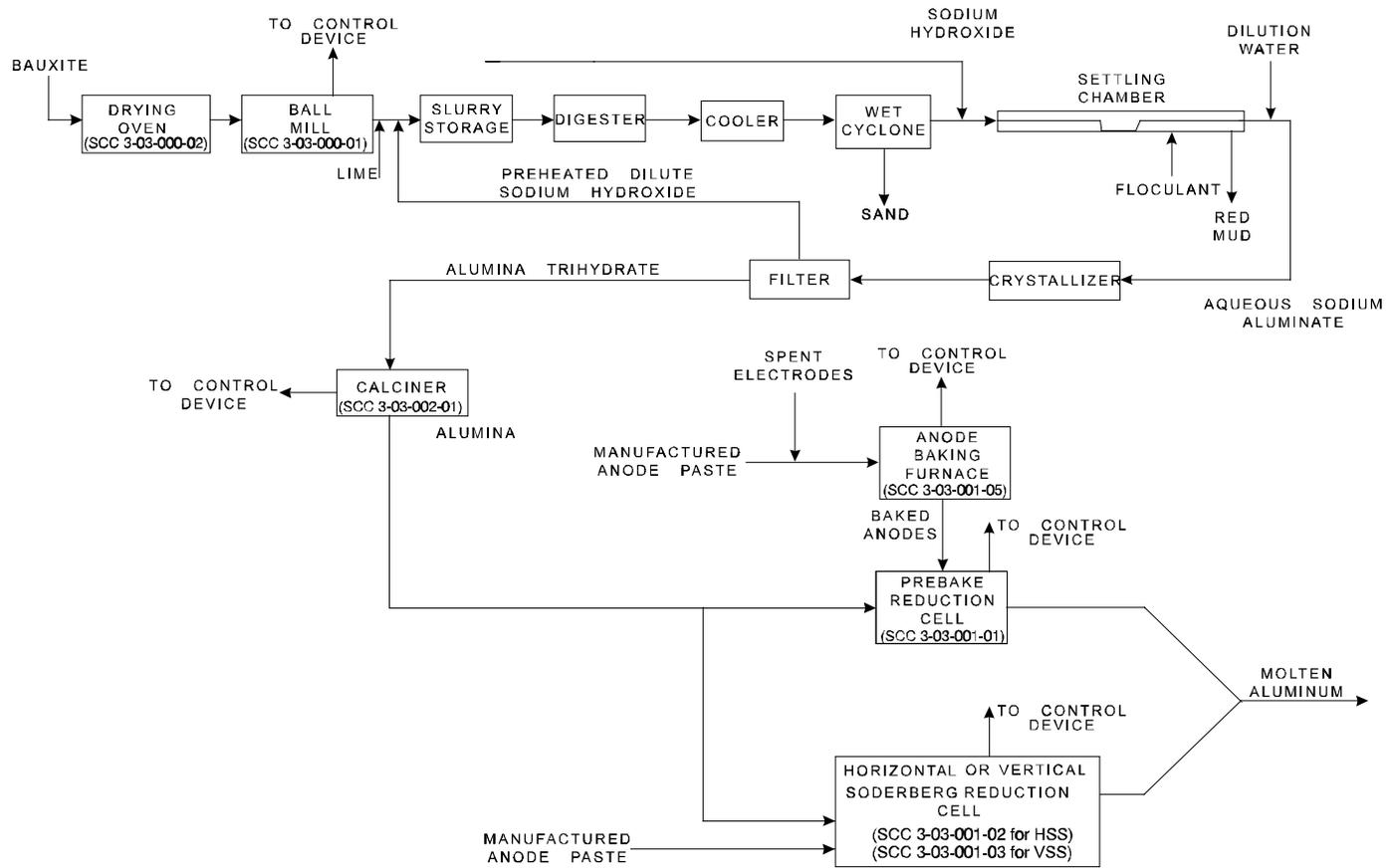


Figure 12.1-1. Schematic diagram of aluminum production process. (Source Classification Codes in parentheses.)

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^{2-9,12}

Controlled and uncontrolled emission factors for total particulate matter, gaseous fluoride, and particulate fluoride are given in Tables 12.1-1 and 12.1-2. Tables 12.1-3 and 12.1-4 give 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 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, volatile organics, and sulfur dioxide (SO₂) from the reduction cells. The source of fluoride emissions from reduction cells is the fluoride electrolyte, which contains cryolite, aluminum fluoride (AlF₃), and fluorospar (CaF₂).

Particulate emissions from reduction cells include alumina and carbon from anode dusting, and cryolite, aluminum fluoride, calcium fluoride, chiolite (Na₅Al₃F₁₄), and ferric oxide. Representative size distributions for fugitive emissions from PB and HSS plants, and for particulate emissions from HSS cells, are presented in Tables 12.1-3 and 12.1-4.

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 SO₂ 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

Table 12.1-1 (Metric Units). EMISSION FACTORS FOR PRIMARY ALUMINUM PRODUCTION PROCESSES^{a,b}

EMISSION FACTOR RATING: A

Operation	Total Particulate ^c	Gaseous Fluoride	Particulate Fluoride	References
Bauxite grinding^d (SCC 3-03-000-01)				
Uncontrolled	3.0	Neg	Neg	1,3
Spray tower	0.9	Neg	Neg	1,3
Floating bed scrubber	0.85	Neg	Neg	1,3
Quench tower and spray screen	0.5	Neg	Neg	1,3
Aluminum hydroxide calcining^e (SCC 3-03-002-01)				
Uncontrolled ^f	100.0	Neg	Neg	1,3
Spray tower	30.0	Neg	Neg	1,3
Floating bed scrubber	28.0	Neg	Neg	1,3
Quench tower	17.0	Neg	Neg	1,3
ESP	2.0	Neg	Neg	1,3
Anode baking furnace (SCC 3-03-001-05)				
Uncontrolled	1.5	0.45	0.05	2,10-11
Fugitive (SCC 3-03-001-11)	ND	ND	ND	ND
Spray tower	0.375	0.02	0.015	10
ESP	0.375	0.02	0.015	2
Dry alumina scrubber	0.03	0.004	0.001	2,10
Prebake cell (SCC 3-03-001-01)				
Uncontrolled	47.0	12.0	10.0	1-2,10-11
Fugitive (SCC 3-03-001-08)	2.5	0.6	0.5	2,10
Emissions to collector	44.5	11.4	9.5	2
Crossflow packed bed	13.15	3.25	2.8	10
Multiple cyclones	9.8	11.4	2.1	2
Spray tower	8.9	0.7	1.9	2
Dry ESP plus spray tower	2.25	0.7	1.7	2,10
Floating bed scrubber	8.9	0.25	1.9	2
Dry alumina scrubber	0.9	0.1	0.2	2,10
Coated bag filter dry scrubber	0.9	1.7	0.2	2
Dry plus secondary scrubber	0.35	0.2	0.15	10

Table 12.1-1 (cont.).

Operation	Total Particulate ^c	Gaseous Fluoride	Particulate Fluoride	References
Vertical Soderberg stud cell (SCC 3-03-001-03)				
Uncontrolled	39.0	16.5	5.5	2,10
Fugitive (SCC 3-03-001-10)	6.0	2.45	0.85	10
Emissions to collector	33.0	14.05	4.65	10
Multiple cyclones	16.5	14.05	2.35	2
Spray tower	8.25	0.15	1.15	2
Venturi scrubber	1.3	0.15	0.2	2
Dry alumina scrubber	0.65	0.15	0.1	2
Scrubber plus ESP plus spray screen and scrubber	3.85	0.75	0.65	2
Horizontal Soderberg stud cell (SCC 3-03-001-02)				
Uncontrolled	49.0	11.0	6.0	2,10
Fugitive (SCC 30300109)	5.0	1.1	0.6	2,10
Emissions to collector	44.0	9.9	5.4	2,10
Spray tower	11.0	3.75	1.35	2,10
Floating bed scrubber	9.7	0.2	1.2	2
Scrubber plus wet ESP	0.9	0.1	0.1	2,10
Wet ESP	0.9	0.5	0.1	10
Dry alumina scrubber	0.9	0.2	0.1	10

^a Units are kilograms (kg) of pollutant/Mg of molten aluminum produced. SCC = Source Classification Code.

^b Sulfur oxides may be estimated, with an EMISSION FACTOR RATING of C, by the following calculations.

Anode baking furnace, uncontrolled SO₂ emissions (excluding furnace fuel combustion emissions):

20(C)(S)(1-0.01 K) kg/Mg (Metric units)

40(C)(S)(1-0.01 K) pounds/ton (lb/ton) (English units)

Prebake (reduction) cell, uncontrolled SO₂ emissions:

0.2(C)(S)(K) kg/Mg (Metric units)

0.4(C)(S)(K) lb/ton (English units)

where:

C = Anode consumption* during electrolysis, lb anode consumed/lb Al produced (English units)

S = % sulfur in anode before baking

K = % of total SO₂ emitted by prebake (reduction) cells.

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

^c Includes particulate fluorides, but does not include condensable organic particulate.

^d For bauxite grinding, units are kg of pollutant/Mg of bauxite processed.

^e For aluminum hydroxide calcining, units are kg of pollutant/Mg of alumina produced.

^f After multicyclones.

Table 12.1-2 (English Units). EMISSION FACTORS FOR PRIMARY ALUMINUM PRODUCTION PROCESSES^{a,b}

EMISSION FACTOR RATING: A

Operation	Total Particulate ^c	Gaseous Fluoride	Particulate Fluoride	Reference
Bauxite grinding^d (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^e (SCC 3-03-002-01)				
Uncontrolled ^f	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	2,10-11
Fugitive (SCC 3-03-001-11)	ND	ND	ND	ND
Spray tower	0.75	0.04	0.03	10
ESP	0.75	0.04	0.03	2
Dry alumina scrubber	0.06	0.009	0.002	2,10
Prebake cell (SCC 3-03-001-01)				
Uncontrolled	94.0	24.0	20.0	1-2,10-11
Fugitive (SCC 3-03-001-08)	5.0	1.2	1.0	2,10
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	2,10
Dry ESP plus spray tower	4.5	1.4	3.4	2,10
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	10
Dry plus secondary scrubber	0.7	0.4	0.3	10

Table 12.1-2 (cont.).

Operation	Total Particulate ^c	Gaseous Fluoride	Particulate Fluoride	Reference
Vertical Soderberg stud cell (SCC 3-03-001-03)				
Uncontrolled	78.0	33.0	11.0	2,10
Fugitive (SCC 3-03-001-10)	12.0	4.9	1.7	10
Emissions to collector	66.0	28.1	9.3	10
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	2,10
Fugitive (SCC 3-03-001-09)	10.0	2.2	1.2	2,10
Emissions to collector	88.0	19.8	10.8	2,10
Spray tower	22.0	7.5	2.7	2,10
Floating bed scrubber	19.4	0.4	2.4	2
Scrubber plus wet ESP	1.8	0.2	0.2	2,10
Wet ESP	1.8	1.0	0.2	10
Dry alumina scrubber	1.8	0.4	0.2	10

^a Units are lb of pollutant/ton of molten aluminum produced. SCC = Source Classification Code.

^b Sulfur oxides may be estimated, with an EMISSION FACTOR RATING of C, by the following calculations.

Anode baking furnace, uncontrolled SO₂ emissions (excluding furnace fuel combustion emissions):

$$20(C)(S)(1-0.01 K) \text{ kg/Mg (Metric units)}$$

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

Prebake (reduction) cell, uncontrolled SO₂ emissions:

$$0.2(C)(S)(K) \text{ kg/Mg (Metric units)}$$

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

where:

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

S = % sulfur in anode before baking

K = % of total SO₂ emitted by prebake (reduction) cells.

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

^c Includes particulate fluorides, but does not include condensable organic particulate.

^d For bauxite grinding, units are lb of pollutant/ton of bauxite processed.

^e For aluminum hydroxide calcining, units are lb of pollutant/ton of alumina produced.

^f After multicyclones.

Table 12.1-3 (Metric Units). UNCONTROLLED EMISSION FACTORS AND PARTICLE SIZE DISTRIBUTION IN ALUMINUM PRODUCTION^a

EMISSION FACTOR RATING: D (except as noted)

Particle Size ^b (µm)	Prebake Aluminum Cells ^c		HSS Aluminum Cells		HSS Reduction Cells	
	Cumulative Mass % ≤ Stated Size	Cumulative Emission Factor	Cumulative Mass % ≤ Stated Size	Cumulative Emission Factor	Cumulative Mass % ≤ Stated Size	Cumulative Emission Factor
0.625	13	0.33	8	0.40	26	12.7
1.25	18	0.46	13	0.65	32	15.7
2.5	28	0.70	17	0.85	40	19.6
5	43	1.08	23	1.15	50	25.5
10	58	1.45	31	1.55	58	28.4
15	65	1.62	39	1.95	63	30.9
Total	100	2.5	100	5.0	100	49

^a Reference 5. Units are kg of pollutant/Mg of aluminum produced.

^b Expressed as equivalent aerodynamic particle diameter.

^c EMISSION FACTOR RATING: C

Table 12.1-4 (English Units). UNCONTROLLED EMISSION FACTORS AND PARTICLE SIZE DISTRIBUTION IN ALUMINUM PRODUCTION^a

EMISSION FACTOR RATING: D (except as noted)

Particle Size ^b (μm)	Prebake Aluminum Cells ^c		HSS Aluminum Cells		HSS Reduction Cells	
	Cumulative Mass % ≤ Stated Size	Cumulative Emission Factor	Cumulative Mass % ≤ Stated Size	Cumulative Emission Factor	Cumulative Mass % ≤ Stated Size	Cumulative Emission Factor
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	2.5	100	10.0	100	98

^a Reference 5. Units are lb of pollutant/ton of aluminum produced.

^b Expressed as equivalent aerodynamic particle diameter.

^c EMISSION FACTOR RATING: C

other particulate matter. Emission factors for these components are not included in this document due to insufficient data. Concentrations of uncontrolled SO₂ 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 SO₂ 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 reacts with the impurities to form HCl, Al₂O₃, 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 Tables 12.1-1 and 12.1-2). These fugitive emissions probably have particulate size distributions similar to those presented in Tables 12.1-3 and 12.1-4.

References For Section 12.1

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