Section VI.B.2.

Guidance by source category: Annex C, Part III Source Categories

Primary aluminium production

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Draft Guidelines on Best Available Techniques (BAT) for Primary Aluminium

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Process Description

Primary aluminium production refers to aluminium produced directly from the mined ore, bauxite. The bauxite is refined into alumina by the Bayer Process, and then the alumina is reduced by electrolysis (the Hall-Héroult Process) into metallic aluminum. This chapter does not cover the secondary aluminium processes, which is covered in **section C.4.3 (Thermal Metallurgical Processes Part II Source Categories)**.

<u>The Bayer Process: Refining Bauxite to Alumina</u>

Bauxite is converted to alumina using the Bayer Process. The bauxite ore is dried, crushed and ground into a powder and mixed with a solution of caustic soda to extract the alumina at elevated temperatures and pressures in digesters. A slurry is produced which contains dissolved sodium aluminate and a mixture of metal oxides called “red mud” that is removed in thickeners. The red mud is washed to recover the chemicals and is disposed. The aluminate solution is cooled and seeded with alumina to crystallize the hydrated alumina in precipitator tanks. The crystals are washed and then calcined in rotary kilns or fluid bed/fluid flash calciners to produce the aluminium oxide or alumina, which is a white powder resembling table salt.

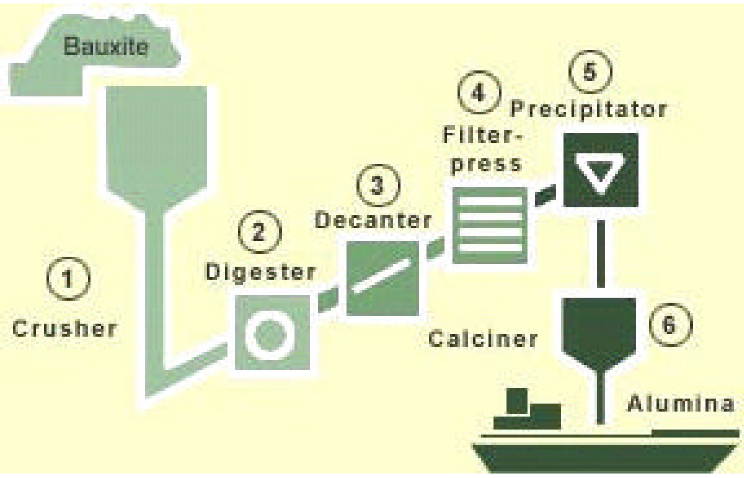

Figure 1: Simplified Flow Sheet for Alumina Production[1]

<u>The Hall-Héroult Process: Reduction by Electrolysis of Alumina to Aluminum</u>

Aluminium is produced from alumina by electrolysis in a process known as the Hall-Héroult Process. The alumina is dissolved in an electrolytic bath of molten cryolite (sodium aluminium fluoride). An electric current is passed through the electrolyte and flows between the anode and cathode. Molten aluminium is produced, deposited at the bottom of the

[1] **Aluminium Association of Canada, http://aac.aluminium.qc.ca/anglais/production/index.html**

electrolytic cell, or “pot”, and periodically siphoned off and transferred to a reverberatory holding furnace. There it is alloyed, fluxed and degassed to remove trace impurities. Finally, the aluminium is cast or transported to the fabricating plants.

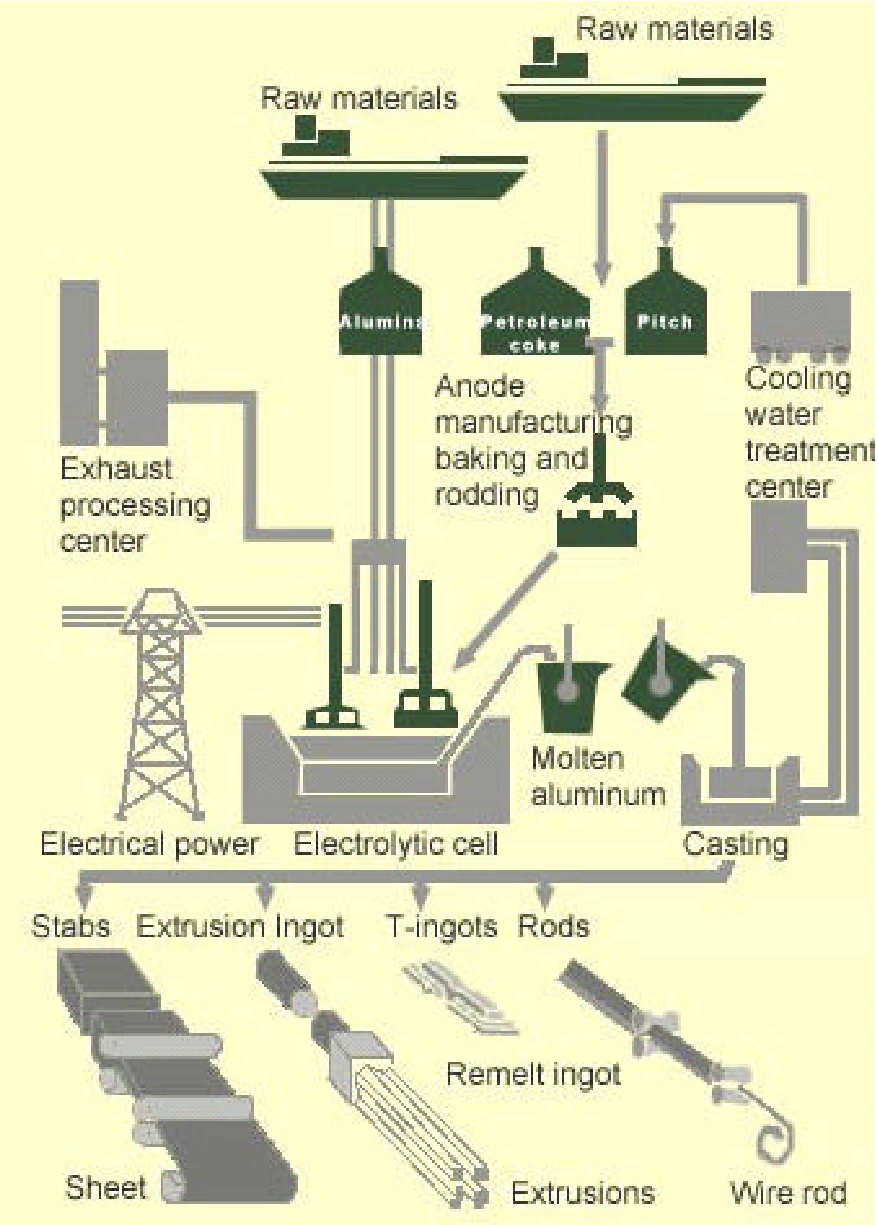

Figure 2: General Schematic of the Electrolytic Process[2]

There are two types of technologies used for the production of aluminium, those using self-baking anodes (Söderberg anodes) and those using pre-baked anodes.

[2] **Aluminium Association of Canada, http://aac.aluminium.qc.ca/anglais/production/index.html**

The older Söderberg anodes are made in-situ from a paste of calcined petroleum coke and coal tar pitch, and are baked by the heat from the molten electrolytic bath. As the anode is consumed, more paste descends through the anode shell in a process that does not require anode changes. Alumina is added periodically to Söderberg cells through holes made by breaking the crust alumina and frozen electrolyte which covers the molten bath. Depending on the placement of the anode studs, these are known as Vertical Stud Söderberg (VSS) or Horizontal Stud Söderberg (HSS) cells or pots. Automatic point feeding systems are used in upgraded plants, eliminating the need for regular braking of the crust.

Pre-bake anodes are manufactured in a carbon plant from a mixture of calcined petroleum coke and coal tar pitch that is formed into a block and baked in an anode furnace. The pre-bake anode production plants are often an integrated part of the primary aluminium plant. The pre-baked anodes are gradually lowered into the pots as they are consumed, and need to be replaced before the entire block has been consumed. The anode remnants, known as anode "butts", are cleaned and returned to the carbon plant for recycling. Depending on the method of feeding the alumina into the electrolytic cells, the cells are called Side-Worked Pre-Bake (SWPB) or Center-Worked Pre-Bake (CWPB). For SWPB cells, the alumina is fed to the cells after the crust is broken around the perimeter. For CWPB cells, the alumina is fed to the cells after the crust is broken along the centreline or at selected points on the centreline of the cell.

The cathode typically has to be replaced every 5 to 8 years because of deterioration which can allow the molten electrolyte and aluminium to penetrate the cathode conductor bar and steel shell. The spent cathode, known as spent pot lining, contains hazardous and toxic substances such as cyanides and fluorides which must be disposed of properly.

Molten alumina is periodically withdrawn from the cells by vacuum siphon and is transferred to crucibles. The crucibles containing liquid metal are transported to the casting plant where the aluminium is transferred to the holding furnaces. Alloying elements are added in these furnaces. Dross ("skimmings") formed by the oxidation of molten aluminium is skimmed off, sealed containers are used to minimize further oxidation of the dross, nitrogen and argon blanketing is used. This is followed by removal sodium, magnesium, calcium and hydrogen. The treatment gas used varies depending on the impurities, argon or nitrogen is used to remove hydrogen; mixtures of chlorine with nitrogen or argon are used to remove metallic impurities.

Sources of Unintentionally Produced POPs

Primary aluminium production is unlikely to be a significant source of dioxin and furan releases although contamination is possible through the graphite-based electrodes[3]. However, release levels are generally thought to be low and the main interest is in the thermal processing of scrap materials[4].

2.1 Emissions of Dioxins and Furans

There is limited information available on dioxins and furans formation from primary aluminium processes. No emission factors have been developed for the industry and available literature suggests that initial emissions testing indicate that dioxins and furans are not considered significant from this sector.

It is unlikely that the Söderberg and pre-baked processes release significantly different emissions per tonne of aluminium produced[5]. Test results on emission sources and abatement units associated with pre-bake anode manufacturing indicate that dioxins are not significant from these sources. However, if chlorine compounds or additives are used, emissions will need to be examined.[6]

Some studies have tested for dioxins in fume from the casting process because the use of chlorine for degassing and the presence of carbon from the combustion gases may lead to the formation of dioxins. Results from primary smelter cast houses have shown that releases are significantly below 1 gram per year.[7] The potential for dioxin formation during the refining processes for both primary and secondary aluminium production has not been fully investigated. It has been recommended that this source be quantified.[8]

2.2 Releases to Land[9]

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[3] AEA Technology Environment, *Releases of Dioxins and Furans to Land and Water in Europe*, prepared for Landesumweltamt Nordrhein-Westfalen, Germany, on behalf of European Commission DG Environment, September 1999, p. 63

[4] UNEP Chemicals, *Standardized Toolkit for Identification and Quantification of Dioxin and Furan Releases*, 1st Edition, Geneva, Switzerland, May 2003, p. 73.

[5] AEA Technology Environment, *Releases of Dioxins and Furans to Land and Water in Europe*, prepared for Landesumweltamt Nordrhein-Westfalen, Germany, on behalf of European Commission DG Environment, September 1999, p. 63.

[6] European Integrated Pollution Prevention and Control Bureau (EIPPCB), *Reference Document on Best Available Techniques in the Non-Ferrous Metals Industries*, Seville, Spain, 2001, p.669.

[7] Ibid., p. 289.

[8] Ibid., p. 318.

[9] New Zealand Ministry for the Environment, *New Zealand inventory of dioxin emissions to air, land and water, and reservoir sources*, March 2000, p. 80 (url: http://www.mfe.govt.nz/publications/hazardous/dioxin-emissions-inventory-mar00.pdf). And references within to the UK Environment Agency report: *A Review of Dioxin Releases to Land and Water in the UK*, Research and Development Publication 3. Environment Agency, Bristol, United Kingdom, 1997.

The production of primary aluminium from ores is not thought to produce significant quantities of dioxins and furans. The UK Review of Dioxin Releases to Land and Water states that there may be the possibility of graphite-based electrodes having some dioxin and furan contamination. Swedish data suggests the spent sludge from the cells may contain 7.8 ng Nordic-TEQ kg^{-1}. However, if the cathode is high purity carbon material and the reduction process does not involve chlorine or chloride materials, it is unlikely that dioxins and furans will be present.

Metal reclaim fines may contain dioxins and furans because chlorine or chlorine based products are used to degas the fraction of the aluminium that is poured into the extrusion billets.

2.3 Research Findings of Interest

Limited information exists on the unintentional formation of dioxins and furans from this sector. It is not considered to be a significant source of releases.

2.4 General Information on Releases from Primary Aluminium Plants[10]

Greenhouse gases are a major pollutant from aluminium production and result from fossil fuel combustion, carbon anode consumption, and perfluorocarbons from anode effects. In addition to greenhouse gases, aluminium smelters also discharge other atmospheric emissions, as well as some solid wastes (spent potliners) and liquid effluents. (p. 3-14)

The use of carbon anodes leads to emissions of sulphur dioxide (SO_2), carbonyl sulphide (COS), polycyclic aromatic hydrocarbons (PAHs) and nitrogen oxides (NO_x). Most of the sulphur in the carbon anode is released as COS, which is not entirely oxidized to SO_2 before being emitted at the potroom gas scrubber stacks. Sulphur emissions are predominately in the form of SO_2 with a minor component of COS. The emission of sulphur gases from aluminium reduction is expected to rise with the increasing sulphur content of petroleum cokes used for anode manufacture. PAHs are the result of incomplete combustion of hydrocarbons found in certain pitch used to form the anodes. The use of prebake anodes has virtually eliminated the emissions of PAHs, mainly associated with Söderberg anodes. The NO_x emissions mainly come from the combustion of fuel in the anode baking furnace. [p. 3-14]

The electrolysis of alumina also leads to the emission of fluorides (particulate fluorides and gaseous HF) and other particulates. The removal of fluorides from the cell gases in

[10] SNC-Lavalin Environment, *Evaluation of Feasibility and Roadmap for Implementing Aluminium Production Technologies that Reduce/Eliminate Greenhouse Gases and Other Emissions*, prepared for Environment Canada, November 2002. pp. 3-14 to 3-16.

modern alumina injection dry scrubber systems is now greater than 99% efficient and the final fluoride emissions from modern prebake smelters are significantly lower. Anode changing and cooling of spent anode butts are the most important sources of fugitive fluoride emissions from an aluminium smelter and these are estimated to 4 to 5 times greater than stack emissions (after the scrubber). [p. 3-16]

The “anode effect” results in generation of perfluorocarbons (PFC) in smelting pots when the concentration of alumina falls below a certain level due to the lack of fresh feed. The carbon anode preferentially reacts with the fluorine in the cryolite solution because there is insufficient oxygen available from the alumina. When this event occurs, CF_4 and C_2F_6 are produced along with a surge in voltage. The amount of PFCs generated depends on the efficiency of feed control in the pot. For pots not equipped with proper controls, PFC emissions from anode effects can be the largest source, accounting for over 50% of the total smelter emissions (on a CO_2-equivalent basis). Practically any point-fed, computer-controlled pot can operate at low anode effect frequency. Older technologies such as HSS and VSS have higher PFC generation rates. These technologies typically do not have individual pot sensing systems and the feed is usually a non-automated bulk system. The process control techniques in modern pre-baked smelters are such that the PFC emissions can be reduced to less than 5% of the total GHG emissions from the smelter. CO_2 emissions from anode consumption are the next largest source for pots without modern controls. [p. 3-10 to 11]

Table 1: Emissions, Effluents, By-products and Solid Wastes from Primary Aluminium Production[11]

Process	Air Emissions [a]	Effluents	By-products and Solid Wastes
Alumina Refining	Particulate	Wastewater containing starch, sand, and caustic	Red mud, sodium oxalate
Anode Production	Particulates, fluorides, polycyclic aromatic hydrocarbons (PAH), SO_2	Wastewater containing suspended solids, fluorides, and organics	Carbon dust, tar, refractory waste
Aluminum Smelting	CO, CO_2, SO_2, fluorides (gaseous and particulate), perfluorocarbons (CF_4, C_2F_6), PAH	Wet air pollution control effluents (wet ESP)	Spent potliners, wet air pollution control wastes, sludges

[a] Excluding combustion-related emissions.

3.0 New Primary Aluminium Plants

[11] Energetics Inc., *Energy and Environmental Profile of the U.S. Aluminum Industry*, prepared by Energetics, for the U.S. Dept of Energy, Office of Industrial Technologies, Maryland, U.S., July 1997. (url: http://www.oit.doe.gov/aluminum/pdfs/alprofile.pdf)

The Stockholm Convention states that when consideration is being given to proposals for construction of a new primary aluminium plant, priority consideration should be given to alternate processes, techniques or practices that have similar usefulness but which avoid the formation and release of the identified substances. [Text taken from Draft Guidelines on BAT for Iron Sintering].

3.1 Alternate Processes to Primary Aluminium Smelting (Emerging Technologies)

There are a number of research initiatives currently underway to produce primary aluminium while concurrently reducing energy consumption and emissions. These include[12, 13, 14, 15, 16]:

- Inert Anodes: Carbon-free anodes that are inert, dimensionally stable, that are slowly consumed, produce oxygen instead of CO_2. The use of inert anodes eliminates the need for an anode carbon plant (and PAH emissions from the process).
- Wettable Cathodes: New cathode materials or coatings for existing cathode materials that allow for better energy efficiency.
- Vertical Electrodes – Low Temperature Electrolysis ("VELTE"): The process uses a non-consumable metal alloy anode, a wetted cathode and an electrolytic bath, which is kept saturated with alumina at the relatively low temperature of 750°C by means of free alumina particles suspended in the bath. This technology could produce primary aluminium metal with lower energy consumption, lower cost, and lower environmental degradation than the conventional Hall-Héroult process.
- Drained Cell Technology: features the coating of aluminum cell cathodes with titanium dibromide and eliminating the metal pad, which reduces the distance between anode and cathode, thereby lowering the required cell voltage and reducing heat loss.
- Carbothermic Technology: Carbothermic reduction produces aluminum using a chemical reaction that takes place within a reactor and requires much less physical space than with the Hall-Héroult reaction. This process would result in significantly

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[12] European Integrated Pollution Prevention and Control Bureau (EIPPCB), *Reference Document on Best Available Techniques in the Non-Ferrous Metals Industries*, Seville, Spain, 2001, p. 335.

[13] SNC-Lavalin Environment, *Evaluation of Feasibility and Roadmap for Implementing Aluminium Production Technologies that Reduce/Eliminate Greenhouse Gases and Other Emissions*, prepared for Environment Canada, November 2002.

[14] Welsh, Barry J., "Aluminum Production Paths in the New Millennium" in JOM, 51 (5) (1999), pp. 24–28. (url: http://www.tms.org/pubs/journals/JOM/9905/Welch-9905.html)

[15] USGS, APPENDIX 2 – ALUMINUM CASE STUDY from: Technological Advancement -- A Factor in Increasing Resource Use, Open-File Report 01-197, Online version 1.02 (url: http://pubs.usgs.gov/of/of01-197/html/app2.htm)

[16] BCS Inc., *U.S. Energy Requirements for Aluminum Production: Historical Perspectives, Theoretical Limits and New Opportunities*, prepared under contract for the U.S. Department of Energy, Energy Efficiency and Renewable Energy, February 2003. p. 41-58.

reduced electrical consumption, and the elimination of perfluorocarbon emissions resulting from carbon anode effects, hazardous spent pot liners, and hydrocarbon emissions associated with the baking of consumable carbon anodes.

- Kaolinite Reduction Technology: The production of aluminum by reduction of aluminum chloride using clays holds appeal because the raw materials are readily available and inexpensive. The thermodynamics also provide high-speed conversion reactions with lower electrical demand and no bauxite residue is produced.

3.2 Performance Requirements for New Primary Aluminium Plants

** The author has found no references on which to base a recommended standard for the releases of dioxins and furans from primary aluminium plants.

4.0 Primary and Secondary Measures

Primary and secondary measures for reducing emissions of dioxins and furans from primary aluminium production processes are outlined below.

*The extent of emission reduction possible with the implementation of primary measures only is not readily known. It is therefore recommended that consideration be given to implementation of both primary and secondary measures at existing plants [**from Guidelines on BAT for Iron Sintering**].*

Note that no specific secondary measures have been developed specifically for the primary aluminium smelters to control the unintentional formation of dioxins and furans. The following measures identified below constitute general measures which may result in lower pollutant emissions at primary aluminium smelters, including releases of dioxins and furans.

4.1 Primary Measures

(Process integrated, holistic measures, primary Pollution Prevention)

Primary measures are understood to be pollution prevention measures that will prevent or minimize the formation and release of the identified substances (particulates, fluorides, polycyclic aromatic hydrocarbons, sulphur dioxide, carbon dioxide, carbon monoxide, and perfluorocarbons – <u>Note that there are no primary measures identified for dioxins and furans</u>). These are sometimes referred to as process optimization or integration measures. Pollution prevention is defined as: *The use of processes, practices, materials, products or energy that avoid or minimize the creation of pollutants and waste, and* *reduce overall risk to human health or the environment.* [**Taken from the Iron Sintering BAT Guidelines**]

For new smelters, using the prebake technology rather than the Söderberg technology for aluminium smelting is a significant pollution prevention measure.[17] The use of centre-worked prebaked cells with automatic multiple feeding points is considered to be BAT for the production of primary aluminium.[18]

Point feeders enable more precise, incremental feeding for better cell operation. They are generally located at the centre of the cell and thereby cut down on the diffusion required to move dissolved alumina to the anodic reaction sites. The controlled addition of discrete amounts of alumina enhances the dissolution process, which aids in improving cell stability and control, minimizing anode effects, and decreasing the formation of undissolved sludge on the cathode. In the jargon of modern commerce, point feeders enable "just-in-time alumina supply" to permit optimum cell operation. Point feeder improvements continue to be made as more accurate cell controllers become available.[19]

Advanced process controllers are also being adopted by industry to reduce the frequency of anode effects and control operational variables, particularly bath chemistry and alumina saturation, so that cells to remain at their optimal conditions.[20]

Primary measures which may assist in reducing the formation and release of the identified substances include:[21]

- o An established system for environmental management, operational control and maintenance.
- o Computer control of the electrolysis process based on active cell databases and monitoring of cell operating parameters to minimise the energy consumption and reduce the number and duration of anode effects.
- o If local, regional or long-range environmental impacts require SO_2 reductions, the use of low sulphur carbon for the anodes or anode paste if practicable or a SO_2 scrubbing system.

[17] World Bank, *Pollution Prevention and Abatement Handbook 1998*, Industry Sector Guidelines – Aluminum Manufacturing, Washington, D.C., 1999.
[18] European Integrated Pollution Prevention and Control Bureau (EIPPCB), *Reference Document on Best Available Techniques in the Non-Ferrous Metals Industries*, Seville, Spain, 2001, p. 325.
[19] BCS Inc., *U.S. Energy Requirements for Aluminum Production: Historical Perspectives, Theoretical Limits and New Opportunities*, prepared under contract for the U.S. Department of Energy, Energy Efficiency and Renewable Energy, February 2003. p. 47
[20] Ibid.
[21] European Integrated Pollution Prevention and Control Bureau (EIPPCB), *Reference Document on Best Available Techniques in the Non-Ferrous Metals Industries*, Seville, Spain, 2001. p. 326, 675-676.

4.2 Secondary Measures

(End of pipe measures)

Secondary measures are understood to be pollution control technologies or techniques, sometimes described as ‘end-of-pipe’ treatments. Note that the following are not considered secondary measures specific to minimization of dioxins and furans releases, but for pollutant releases generally.

The following measures have been shown to effectively reduce releases from primary aluminium production and should be considered at BAT:[22]

- Feed preparation: Enclosed and extracted grinding and blending of raw materials, fabric filters for abatement.
- Complete hood coverage of the cells, which is connected to a gas exhaust and filter. The use of robust cell covers and adequate extraction rates. Sealed anode butt cooling system.
- Better than 99% fume collection from cells on a long term basis. Minimization of the time taken for opening covers and changing anodes.
- Gases from the primary smelting process should be treated to remove dust, fluorides and HF using an alumina scrubber and fabric filter. The scrubbing efficiency for total fluoride should be >99.8%, and the collected alumina used in the electrolytic cells.
- Use of low-NO_x burners or oxy-fuel firing. Control of firing of furnaces to optimize the energy use and reduce PAH and NO_x emissions.
- If there is an integrated anode plant the process gases should be treated in an alumina scrubber and fabric filter system and the collected alumina used in the electrolytic cells. Tars from mixing and forming processes can be treated in a coke filter.
- Destruction of cyanides, tars and hydrocarbons in an afterburner if they have not been removed by other abatement techniques.
- Use of wet or semi-dry scrubbing to remove SO_2 if necessary.
- Use of bio-filters to remove odorous components if necessary.
- Use of sealed or indirect cooling systems.

5.0 Summary of Measures

The following tables present a summary of the measures discussed in previous sections.

Table 2: Measures for New Primary Aluminium Production Plants

Measure	Description	Considerations	Other Comments
Alternate	Priority should be given to alternate	Examples include:	These processes are

[22] Ibid. p. 326 and 675-676.

Processes	processes with less environmental impacts than tradition primary aluminium production plants.	o Inert anodes o Wettable cathodes o Vertical Electrodes – Low Temperature Electrolysis o Drained Cell Technology o Carbothermic Technology o Kaolinite Reduction Technology	still in the development phase.
Prebake technology	The use of centre-worked prebaked cells with automatic multiple feeding points is considered BAT.		
Performance Requirements	New primary aluminium production plants should be required to achieve stringent performance and reporting requirements associated with best available technologies and techniques.	o Consideration should be given to the primary and secondary measures listed below in the following table.	No performance requirements have been determined for releases of dioxins and furans from primary aluminium plants.

Table 3: Summary of Primary and Secondary Measures for Primary Aluminium Production Plants

Measure	Description	Considerations	Other Comments
Primary Measures			
Environmental management system, operational control and maintenance			
Computer controlled process and monitoring	To minimise energy consumption and reduce number and duration of anode effects.	o	
Feed selection: Use of low sulphur carbon for anodes or anode paste. Use of	To control sulphur dioxide emissions, if necessary.	o SO_2 scrubbing system may be used.	
Secondary Measures			
Feed preparation: Enclosed grinding and blending of raw materials. Use of fabric filters.	To prevent the releases of particulates.		
Complete hood coverage of cells	The use of hoods that completely cover cells to collect gases to the exhaust and filter.		

Fume collection and treatment	Fume collection efficiency should be greater than 99%. Gases should be treated to remove dust, fluorides and HF using an alumina scrubber and fabric filter.		The time taken for opening the covers and changing the anodes should be minimized.
Low NO_x burners Oxy-fuel firing	The firing of the furnace should be optimized to reduce PAH and NO_x emissions.		
Alumina scrubber	Process gases from anode plant should be treated in an alumina scrubber and fabric filter system.		The alumina should be used in the electrolytic cells. Tars can be treated in a coke filter
Afterburner	To destroy cyanides, tars and PAHs if not removed by other abatement.		
Wet or semi-dry scrubbing	To remove SO_2 if necessary.		
Bio-filters	To remove odorous components if necessary.		

6.0 Performance Standards

I have found no existing performance standards or timelines for the release of dioxins and furans from primary aluminium plants.

7.0 Performance Reporting

The recommended performance reporting for dioxins and furans should be similar to that of other existing sectors.