Reduction of Emission from Aluminium Industries and Cleaner Technology

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ABSTRACT

Aluminium metal is produced by electrolytic reduction of alumina in cells lined with carbon blocks. During the process of smelting different gaseous emissions like PFC (per fluorocarbon), HF, PAH (poly aromatic hydrocarbon), CO_2, SO_2, particulate matters etc. occur in to the atmosphere. The concentration of emission from a cell depends upon the type of cell, bath chemistry, scrubbing system and gas cleaning equipment used. These emissions cause severe environmental damages such as global warming and disease like fluorosis, cancer, asthma, emphysema, bronchitis etc. Through the development of newer technologies like, introduction of prebake technology, use of non-consumable (inert) anode, use of computer controlled and point feeding of alumina to the cell to control the frequency and duration of anode effects, use of low carbon pitch to replace tar, use of pollution monitoring and control equipment etc., there is a significant reduction in the emission levels. This paper deals with the factors influencing the generation of these emissions and its reduction through the development of various cleaner technologies. Use of pollution control equipment and other remedial measures to minimise the environmental pollution are also discussed.

Key Words : Cleaner technology, aluminium, smelter, emissions, remedial measures.

INTRODUCTION

The Hall Heroult process for electrolytic reduction of alumina to produce aluminium was invented in 1886. In this process alumina is dissolved in an electrolytic bath of molten cryolite within a large carbon or graphite lined steel container known as pot. An electric current is passed through the electrolyte at low voltage but at very high current, typically about 150,000 amp. The electric current flows between a carbon anode (+) made of petroleum coke and pitch and a cathode(-) formed by a thick carbon or graphite lining of the pot. Molten aluminium is deposited at the bottom of the pot and siphoned off periodically to be taken to a holding furnace. Since that time, process has changed a lot and a modified process is found in todays smelter.

During the smelting process different gaseous products are emitted to the atmosphere. Emission of these gases vary from cell to cell depending on the technology. Some of these emissions contribute to global warming. The most challenging task for today's aluminium industry is how to reduce the emission by adopting new technologies, as these cause the environmental damage. This aspect has been receiving more attention recently due to stringent environment laws of the present days.

This paper deals with the various emissions from aluminium smelters and their reduction through technological development and other remedial measures to control the environmental pollution.

MAJOR EMISSIONS

PFC and HF

During aluminium production several Perfluorocarbon (PFC) gases are evolved. These are not generated during normal smelting conditions. They are only produced during brief upset conditions which is solely related to most specific and intermittent phenomenon in the electrolytic process referred to as the anode effect of the cell. These conditions occur when the level of the dissolved alumina in the cell drops too low and the cryolytic bath itself begins to undergo electrolysis. The main gases are CF_4 and C_2F_6 but also other PFC gases like C_3F_6 and C_3F_8 may be formed in minor quantities[1].

$$4Na_3AlF_6 + 3C \quad = \quad 4\,Al + 3NaF + 3CF_4 \quad 2.55V\ (967°C) \quad \ldots \quad (1)$$

$$4\,Na_3AlF_6 + 4C \quad = \quad 4\,Al + 12NaF + 2\,C_2F_6 \quad 2.77V\ (967°C) \quad \ldots \quad (2)$$

Depending on the technology, emission of these gases vary. Also the frequency and duration of anode effect determine the emission of PFC's. With the development of new technologies the emission level of PFC's decreases (Table-1). It is estimated that C_2F_6 has much more global warming potential than CF_4 [2].

Table 1 : CF_4 and C_2F_6 emissions from aluminium smelter per tonne of aluminium production[3]

Plants	Period	Emission in kg/tonne
1st generations	1950-1955	12.0 - 15.0
2nd generations	1955-1975	2.0 - 6.0
3rd generations	1975-today	0.3 - 1.0

Apart from PFC's, HF gas is also formed from two principal sources. One of them is during the reaction occurring in the bath between AlF_3 and moisture. The other is hydrolysis of $NaAlF_4$ vapour present above the bath surface. Excess emission of HF is due to the chemical process occurring in the filter dust, involving particulate fluoride compounds originating in the electrolytic bath and moisture present in the pot gas.

$$2AlF_3 + 3H_2O = Al_2O_3 + 6HF \quad \ldots \quad (3)$$

$$3NaAlF_4(g) + 3H_2O(g) = Al_2O_3 + Na_3AlF_6(s) + 6HF(g) \quad \ldots \quad (4)$$

PFC reduction

Research efforts have been continuing on the better understanding of process parameters related to PFC generation as well as their reduction. Restructuring new and improved gas cleaning equipment and continuous improvements in the smelter operation have contributed to considerable reduction of the fluoride emissions from the aluminium smelter.

Technologies followed

Today smelter uses two types of electrode technologies : Soderberg and Prebaked.

1) Soderberg technology uses a continuous anode which is delivered to the cell (pot) in the form of a paste and which bakes in the cell itself. The Soderberg technology has two variants based upon how the electricity is introduced to the cell, namely Vertical Stud Soderberg (VSS) and Horizontal Stud Soderberg (HSS).
2) Prebaked technology uses a multiple anode in each cell which are prebaked in a separate facility and attached to rods that suspend the anode in the cell. New anodes are exchanged for spent anodes. Prebake technology has two variants referring to how alumina is added, namely centre worked (CWPB) and side worked (SWPB).

The newest primary smelter uses the centre worked prebake technology. This technology provides use of multiple point feeders and other computerised controls for precise alumina feeding. A key feature of CWPB plants is the closed circuit nature of the process. Fugitive emissions from these cells are very low which is less than 2% of the generated emissions. The balance of the emission is collected inside the cell itself and carried away to very efficient scrubbing system.

Efforts have been made to reduce the emission levels in aluminium plants of Asian countries, Eastern Europe and Russia. These regions tend to rely on older Soderberg technology which offers significant greenhouse gas reduction potential[3].

US aluminium industry achieved 46% reduction of PFCs (Fig.1) from 1990 to 1998 through the technical improvement like reduction of frequency and also to some extent the duration of the anode effect in pot line cells[3]. Significant progress has also been made in improving environmental performance through the technological development (Table-2).

Table 2 : Emission of CF_4 with different type of cell technology[3]

Technology type	Kilograms CF_4 per tonne of aluminium produced 1990	1997
CWPB	0.36	0.15
VSS	0.70	0.45
SWPB	1.88	1.34
HSS	0.36	0.46

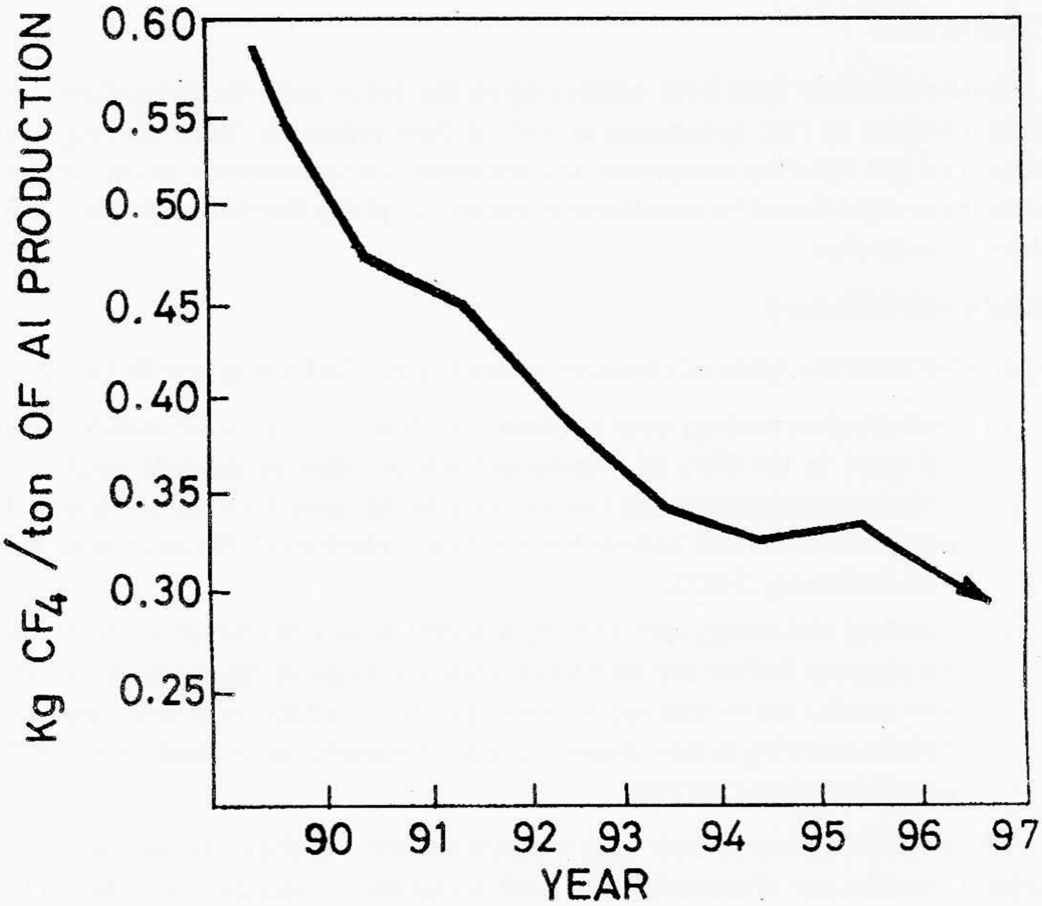

Fig. 1 : Emission of CF_4 in aluminium production between 1990-97

At present gaseous fluoride has been reduced to a level of 0.8 kg/t of Al production in Soderberg cells and 0.06 kg/t of Al for Prebake cells. These gases are only observed during anode effect. The best way to reduce CF_4 emission is to reduce anode effect frequency and the duration of anode effect.[1]

Table 3 : Total CF_4 emissions in different cells

Pot lines	CF_4 gas emissions kg/t Al	Anode effect duration (Minutes)	Anode effect frequency (AE/cell.day)
Soderberg	0.80±0.20	4.0	2.4
Prebake	0.06±0.02	3.8	0.13

In prebake potlines 97-99% of anode gas goes through the gas duct but in the Soderberg series more of the anode gas is emitted into the pot room and passes through roof ventilators.

Online monitoring of the common exhaust from 40 pots of a commercial pot line[4] shows that the average emission rates from the potline over 510 pot days is 0.2 kg CF_4/tonne Al and 0.02 kg C_2F_6/tonne of Al.

Gas collection and cleaning operation have reduced these emission level drastically in the last 30-40 years. As chemical reaction in pot gas fume contribute significantly to the dry scrubber HF emissions, the properties of the dust cake on the surface of the filter bag are important to minimise the impact of the chemical HF emission. In traditional dry scrubber the filter cake consists of fumes and HF-enriched fine particulate alumina, which implies that the cake has a low adsorption capacity. In current scrubber the properties of filter cake has been improved through the introduction of fresh alumina in the filter bag which enhance the potential for removing chemically emitted HF. It improved adsorption of pot gas HF and reduce dust emission[5].

In modern smelters, exhaust from pot is captured by an advanced exhaust system and routed to gas treatment centres where alumina is injected into the gas stream and the fluoride is adsorbed by the alumina. This fluoride enriched alumina is recovered and distributed to the electrolytic pots. Continuous monitors are used to measure the efficiency of gas treatment centres.

PAH

Poly aromatic hydrocarbon (PAH) emissions from aluminium smelter have strongly focused during last decade. Anodes used in the electrolytic process are made from petroleum coke and pitch. Baking of pitch contained in the anode is the source of PAH. Tables 5 & 6 show the emission level of PAH from a Norwegian Aluminium Industry[6]. Data were obtained by measurement in anode paste plant, baking furnace, Soderberg smelter and Prebake smelter.

Table 5 : PAH level in work place atmosphere (Soderberg)

Job group	PAH-exposure (μg/m³)
Foreman	10
Cell operator	16
Tapping	9.0
Bath control	7.0
Burner cleaning	8.0
Stud pulling	14
Stud maintenance	12
Rack raising	8.0

Table 6 : PAH emission from paste plant mixers (Soderberg)

Paste plant	Particulate (mg/m³)	Gaseous (mg/m³)	Total (kg/h)
Cathode line	23.4	8.5	0.19
Soderberg line M1	164.0	34.0	0.16
M2	5.0	2.4	0.11
Prebake line	26.3	3.7	0.18

M1 - Mixer 1
M2- Mixer 2 (briquette forming)

In paste plant there are several production steps that can cause emission of PAH. These are handling of solid pitch (particulate), handling of liquid pitch (gaseous) and emission of aerosols and vapours from paste mixture.

Table 7 : PAH in work place atmosphere (prebake)

Job group	PAH exposure (μg/m³)
Anode rodding	2.0
Anode changing	0.5

Table 8 : Roof top emission of PAH from potrooms

Pot room	Particulate (μg/m³)	Gaseous (μg/m³)	Total (μg/m³)
Soderberg with dry anode	140	110	250
Prebake with collar paste	14	12	26
Prebake	3	–	3

In the electrolysis, the PAH-problem is mainly related to Soderberg smelter. This is of course due to the fact that the Soderberg anodes are actually calcined during the electrolysis process, thus allowing the tar fumes including PAH to emit from the top of the anode, and through cracks in the anode and into the primary gas collection system. In addition to this, the stud pulling will also cause a severe emission of PAH. In case of prebake anode the amount is insignificant and is taken care of in anode baking furnace. There are 40-50 types of PAH present in coal tar pitch[7]. Some of them have carcinogenic effects in animal tests. Emission of PAH from plants using Soderberg technology is a great problem. Efforts are being made to reduce the emission level by modifying the characteristics of the anode paste and operation methods. Traditional pitch is made from carbon tar. In the new pitch, the PAH materials have been replaced with petroleum by-products. Anode materials with lower pitch content was developed with new varieties of pitch which generates smaller quantities of PAH. Replacement of Soderberg anode with vertical stud have much lower PAH emission. The scrubbing systems are also in the process of being modified for improving their tar collection efficiency.

CO_2 Emission

CO_2 are emitted from two sources, anodes of petroleum coke and pitch when they are consumed in the process and generation of power which is used in the electrolytic process. CO_2 is produced as per the following primary reaction in smelting.

$$1/2\ Al_2O_3 + 3/4x\ C = Al + 3/4(2-1/x)\ CO_2 + 3/2(1/x\ -1)CO \quad \ldots \quad (5)$$

With 100% current efficiency the CO_2 produced is 1.2 tonne per tonne of aluminium production. Practically, the best operation in smelter restrict the CO_2 emission only to 1.15 tonne per tonne of aluminium. If the emission from the anode paste plant are also included the total value goes to 2 tonne per tonne of Al. Considering the present Al production at about 26 million tonnes per year the total CO_2 produced goes to about 50 million tonnes per year[2].

Table 9 : CO_2 emissions during aluminium electrolysis by various types of power plants (kg/ tonne of Al)[8,9]

Type of power plant	CO_2 from electrolysis	CO_2 from power plant	Total CO_2
Hydroelectric	1740	0	1740
Gas fired	1740	6160	7900
Coal fired	1740	15400	17100

Assuming energy consumption of 15.4 kWh/kg of Al and anode consumption of 475 kg/t of Al, gas fired plant emits 0.4 kg CO_2 /kWh and coal fired power plant emit 1 kg CO_2 /kWh.

Table 10 : Emission of CO_2 from Indian aluminium plants

Company	Location	CO_2 emission in tonne/tonne Al production	Technology/Process
NALCO	Angul, Orissa	17.31	Prebaked, PF, 180 kA
HINDALCO	Renukoot, UP	16.47	Prebaked, PF, 60-65 kA
INDAL	Alupuram, Kerala Hirakud, Orissa Belgaum, Bangalore	18.85	Soderberg, HS, 50 kA -do- -do-
BALCO	Korba, MP	19.29	Soderberg, VS, 100 kA
MALCO	Metur (T.N)	-	Soderberg, VS, 50 kA

SO_2 Emission

The major sources of sulphur in aluminium electrolysis are organic sulphur compounds in the petroleum coke and coal tar pitch used in the anode materials[2]. These compounds react with alumina in the bath to form SO_2 (g). Some smelters use sea water or a basic aqueous solution in wet scrubber to treat the SO_2 containing anode gases.

Table 11 : SO_2 level of an Indian aluminium plant[10]

Location point	SO_2 level		
	Minimum (ppm)	Maximum (ppm)	Average (ppm)
1	178	295	242
2	53	278	111
3	69	363	191

1, 2 - Sampling point 6m either side of electrolytic pot inside cell house

3 - Sampling point 6m height above electrolytic pot (roof level)

CONTROL OF EMISSIONS

As the above emissions have various undesirable effects the aluminium industries have developed different types of scrubbers (Fig.2) and emission control technology.[5] Most of the smelters have dry fume control and fluoride recovery system. In addition, several smelters are upgrading and retrofitting existing fume control system. The hooder prebake pots have gone through an evolution from side break, centre break/centre fed to point feeding. The tendency towards operation with more acidic bath results in high fluoride evolution. This again increases the requirement on performance of the dry scrubbing system as well as the holding efficiency and pot room discipline. In older smelter, addition of lithium in electrolytic bath reduces the quantity of fluoride emission. It is treated in wet scrubber before being exhausted to atmosphere.

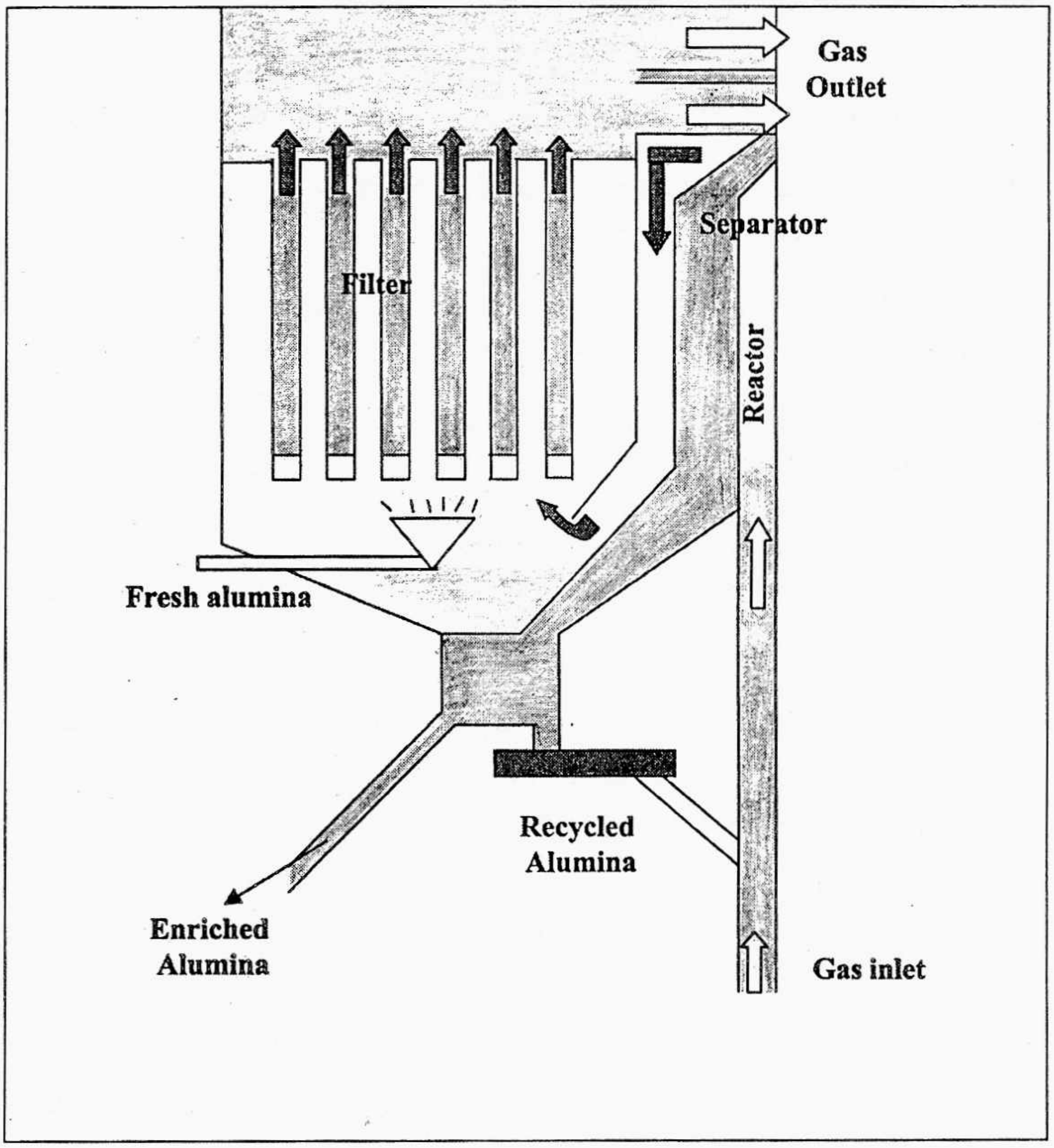

Fig. 2 : Abart Dry Scrubber

A new technology like the use of inert anodes[11] made up of cermets and a composite material made from a mixture of metal oxide and alloys instead of traditional baked carbon anode are used to reduce the CO_2 level. Such anodes are dimensionally stable, and when used in smelting process would produce oxygen as opposed to the CO_2 produced for conventional smelter .

Replacing anode carbon with zirconia tubes carrying natural gas and application of DC voltage would draw oxygen through the tubes to oxidize the natural gas, which is mostly methane. This would eliminate fluorocarbon production and cut CO_2 emission by half.

CONCLUSIONS

From the above discussion it emerges that the following measures may be helpful for the reduction of hazardous emissions from aluminium industries.

i) Preference should be given to Prebake Technology rather than Soderberg Technology.

ii) Use of computer control and point feeding of aluminium oxide to the centre line of the cell are necessary to control the bath composition and limit the anode effects.

iii) Baking furnace gases may be used for energy recovery.

iv) Use of dry scrubbing system with aluminium oxide as the adsorbent for control of gases from the cell and from anode bake oven is necessary.

v) Fabric filters or ESP for controlling particulate matters may be used.

vi) Use of low sulfur tar for baking anodes will help control suphur dioxide emissions.

vii) Use of inert anode in place of carbon anode will reduce the emission.

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