ADDRESSING FUTURE CHALLENGES TO REDUCE PFCS EMISSIONS FROM ALUMINUM SMELTERS

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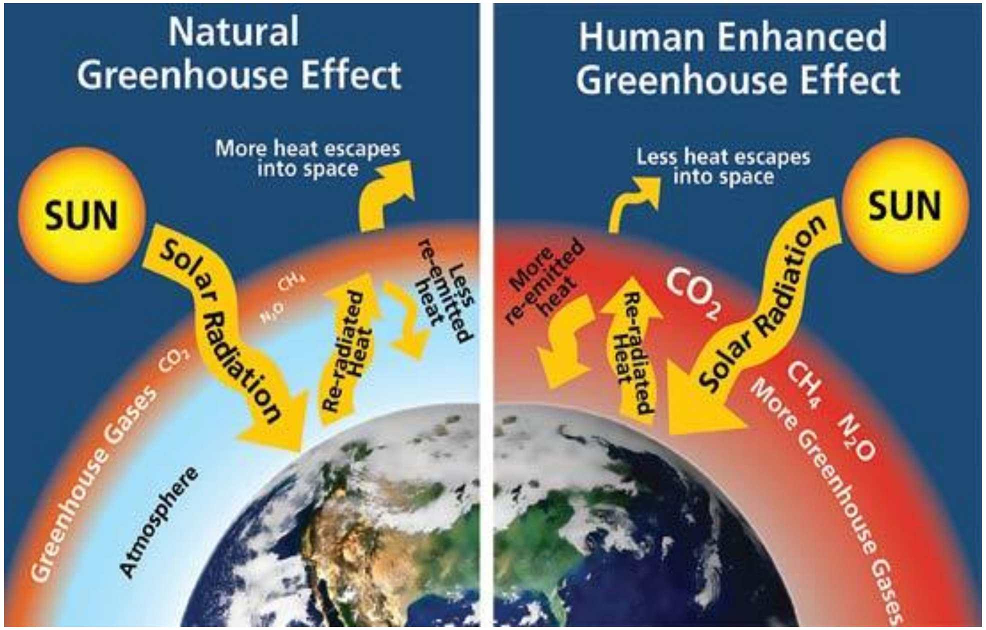
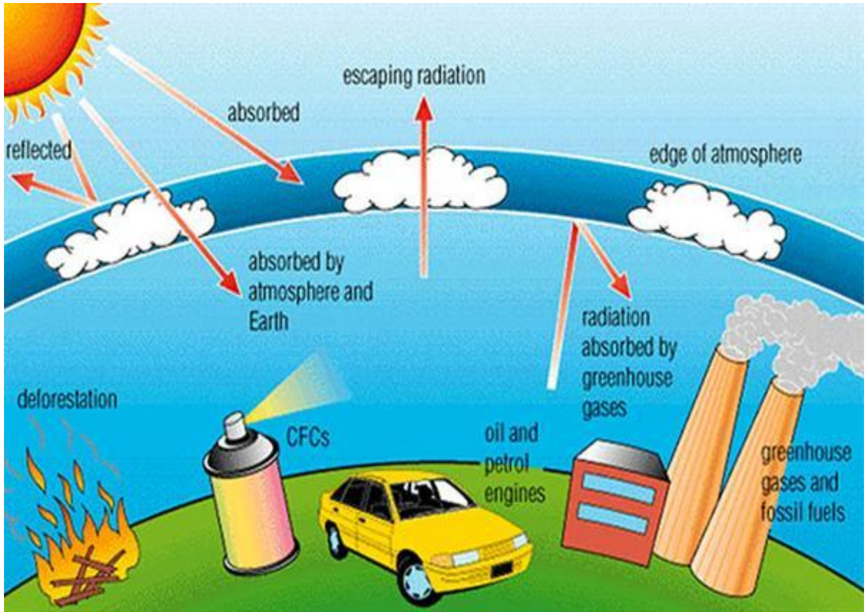


- If the Earth is in a thermal steady state: **T= 256 K**
- Real average: **288 K**.
- This difference is due to **natural greenhouse effect**
- Natural greenhouse gases: **H_2O, CO_2, N_2O, CH_4**
- Human Enhanced Greenhouse effect: **Excessive amounts** of natural GHG gases and **xenobiotic** GHG gases

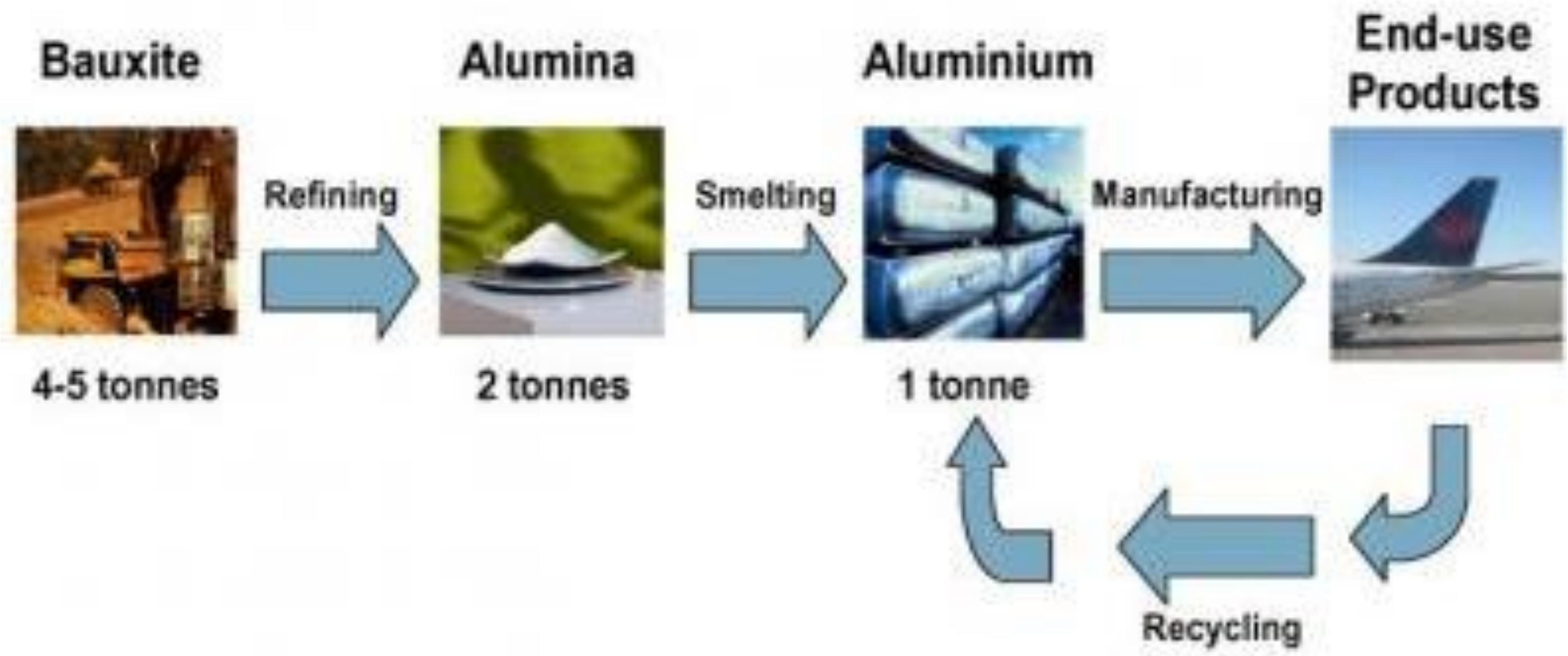
Component	Greenhouse efficiency per molecule
CO_2	1
CH_4	21
N_2O	206
CFC-11	12400
CFC-12	15800



Primary sources of greenhouse gas emissions

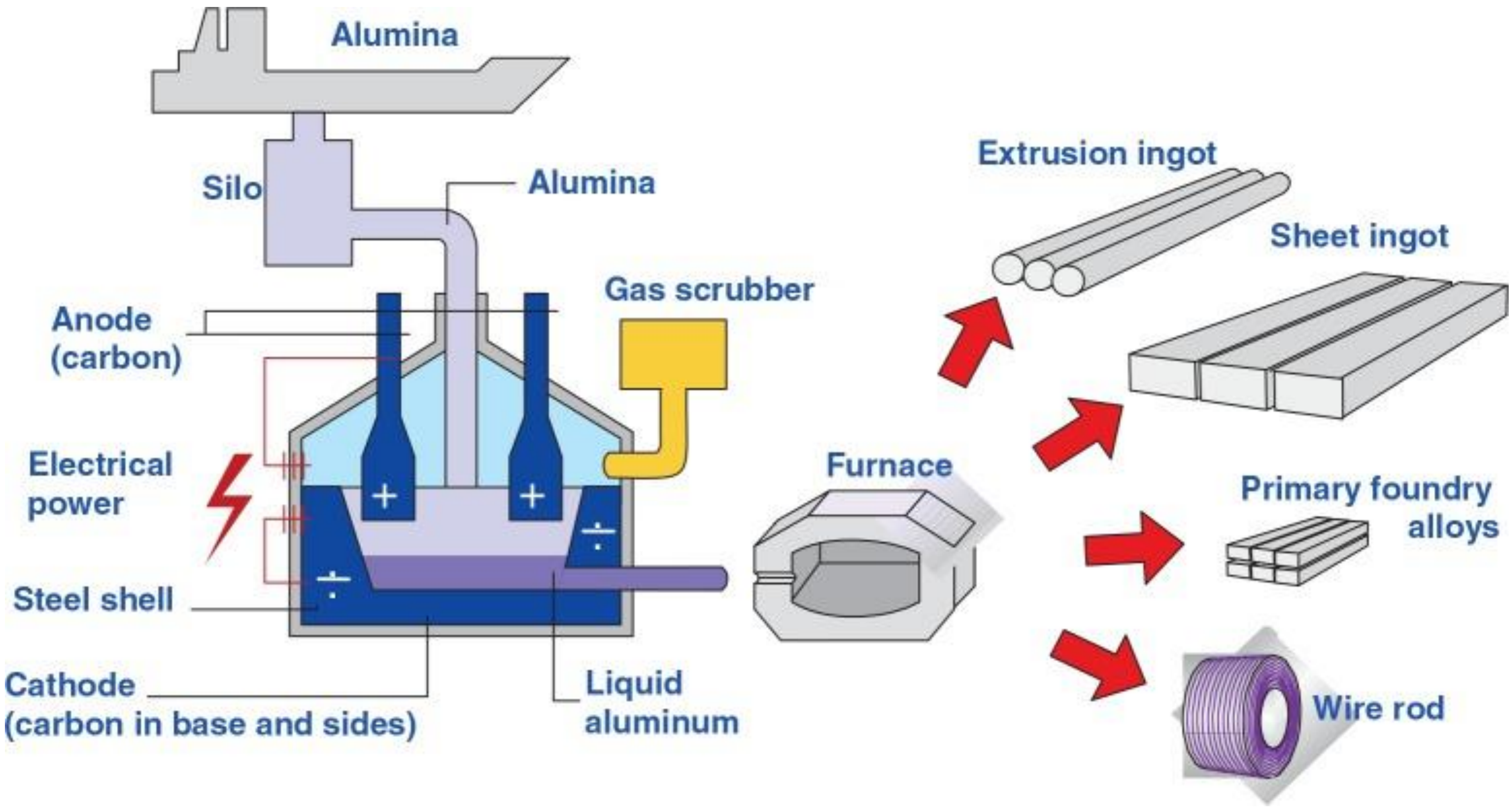
- Electricity production (**31%** of 2013 greenhouse gas emissions) - Electricity production generates the largest share of GHG emissions.
- Transportation (**27%** of 2013 greenhouse gas emissions) - GHG emissions from transportation primarily come from burning fossil fuel.
- Industry (**21%** of 2013 greenhouse gas emissions) – GHG emissions from industry primarily come from burning fossil fuels for energy from certain chemical reactions necessary to produce goods from raw materials.
- Commercial and Residential (**12%** of 2013 greenhouse gas emissions) – GHG emissions arise primarily from fossil fuels burned for heat, the use of certain products that contain greenhouse gases.
- Agriculture (**9%** of 2013 greenhouse gas emissions) – GHG emissions from agriculture come from livestock and rice production.

Aluminum production cycle



- 2 main inputs in primary aluminum : alumina and energy
- 2 main features of the production process:
  - Energy use
  - Environmental impact

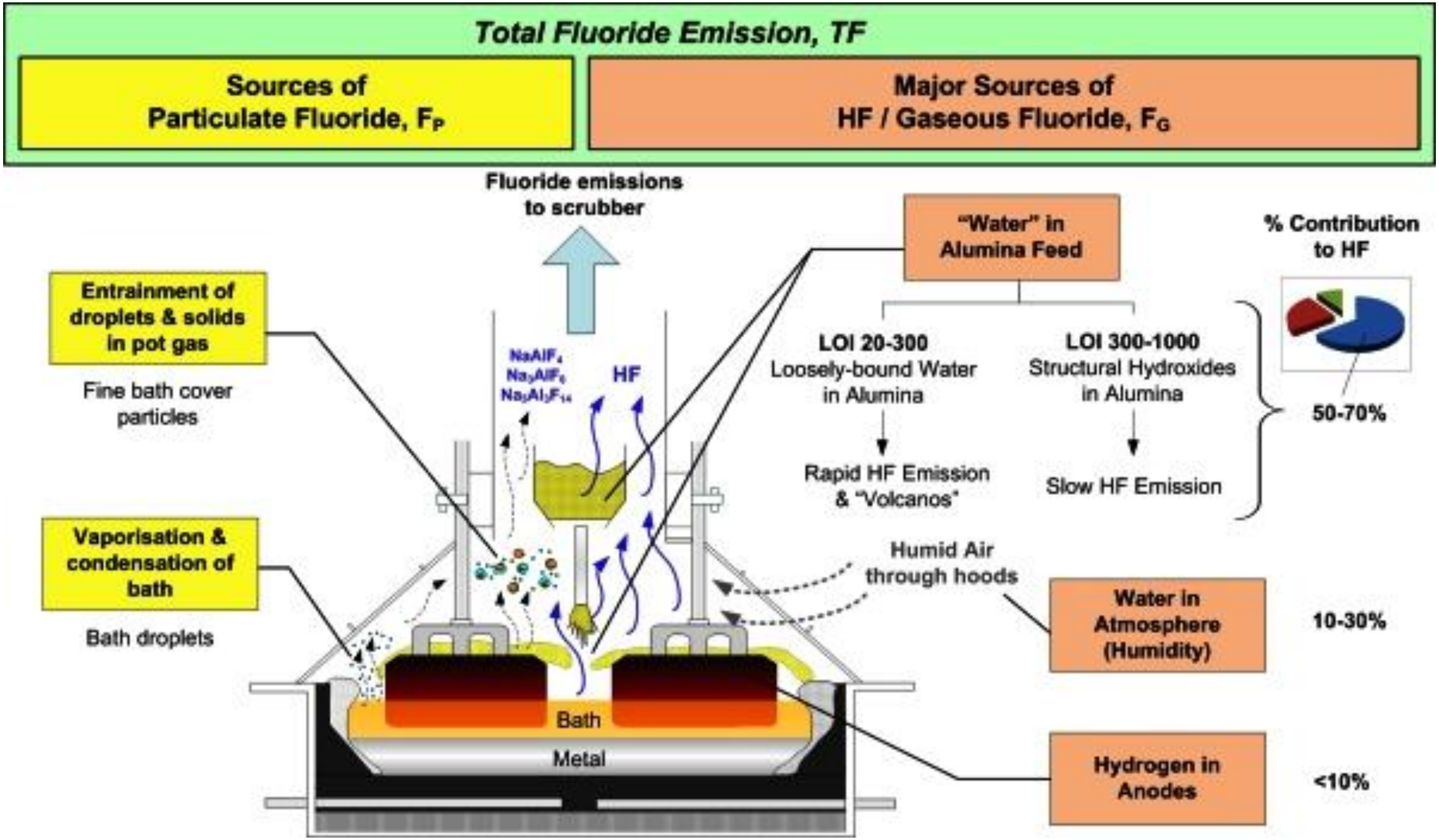
Aluminum production cycle



Air emissions From Aluminium Industry

- **Fluorides (HF & particulate)** are mainly emitted from the pots during interventions in the pots (like anode changing).
- **Sulfur dioxide (SO_2)** is emitted mainly from oxidation of the sulfur content in the anodes.
- **Dust** is mainly emitted from **pot lines** and material **handling** systems.
- **Anode production** is a source of **polyaromatic hydrocarbons** (**PAH)**, but more efficient systems have **reduced** these **emissions** to a minimum.

Fluoride emissions from aluminium smelters



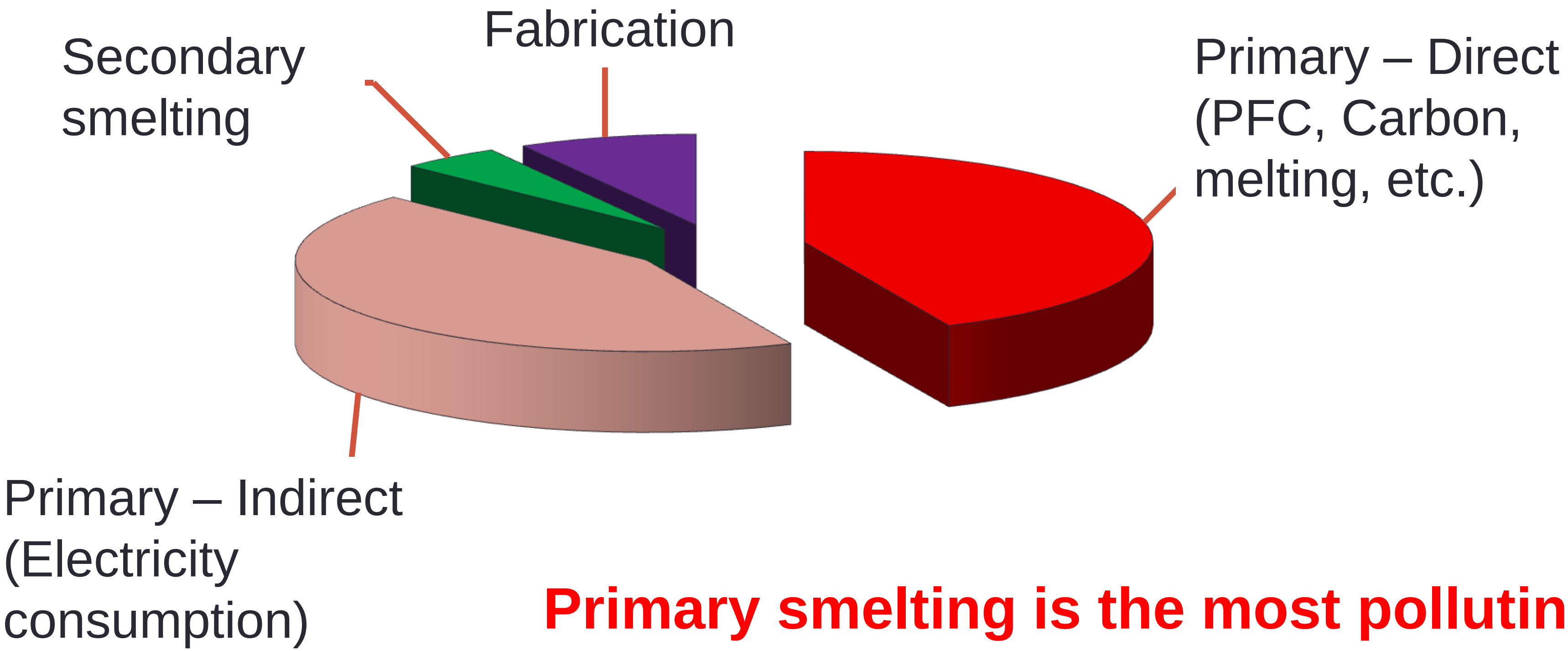
Fluoride emissions from aluminium smelters

- **Generation** of unwanted **fluoride by-products** from the aluminium smelting process is an **unfortunate reality** of the current state technology.
- The **release of these fluorides** into the potrooms and surrounding environment is **unacceptable** and must be **minimized**.
- There are **legal**, **health**, **environmental** and **operational** performance issues which drive all smelters to consider **effectively**.

GHGs Emissions from Aluminium production

- **The major environmental impact** of refining and smelting is greenhouse gas (**GHG**) emissions.
- Greenhouse gas **emissions** in the production of primary aluminium come from processes such as **coking**, **anode production** and **consumption**, and **electrical generation**.
- The greenhouse gases resulting from aluminum production include, among others, **carbon dioxide** (CO_2), and **perfluorocarbons** (PFCs).

GHGs emissions from Aluminium industry



Primary smelting is the most polluting stage of aluminum production

Primary Aluminium production and PFCs emissions

- Primary aluminium is produced using the **Hall-Héroult electrolytic** process.
- In this process, the **smelting pot** itself acts as the **electrolysis cell** during the reduction process.
- The pot itself forms the **cathode**, while the **anode** consists of one or more **carbon** blocks suspended in it.
- Molten aluminium is evolved while the anode is consumed in the reaction as follows:

$$2\ Al_2O_3(sl) + 3\ C(s) \rightarrow 4Al(l) + 3\ CO_2(g)$$

GHGs From Primary Aluminium Production

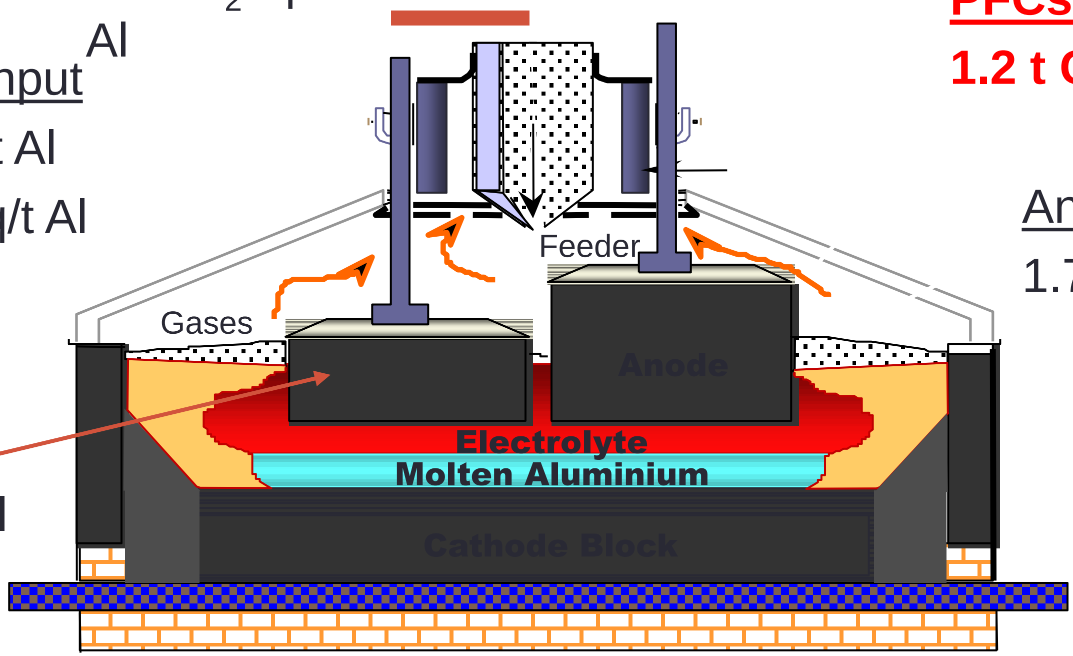
CO_2
Alumina mining & refining
2 t CO_2eq/t Al

CO_2
Electricity Input
15.6 MWh/t Al
4.8 t CO_2eq/t Al

CF_4 and C_2F_6
PFCs Emissions
1.2 t CO_2eq/t Al

CO_2
Anode Carbon
1.7 t CO_2eq/t Al

CO_2
Anode fabrication
0.3 t CO_2eq/t Al



PFCs are potent GHGs, 5,000 to 10,000 times more powerful than CO_2

Global average about 11 t CO_2 eq/t Al

Primary Aluminium production and PFCs emissions

- The **aluminium production** process is the largest **anthropogenic source** of emissions of two PFCs: **CF_4** and **C_2F_6**.
- **PFCs emissions** are expected to **increase** at a slower rate than aluminium production because PFCs **emission factors** are expected to **decrease over time**.
- Reductions in **PFCs emission factors** are anticipated by using **modernized** smelter technologies
- Large **efforts** to **reduce** PFCs **emissions** from aluminium smelting.

Primary Aluminium production and PFCs emissions

Species	Chemical Formula	Lifetime (years)	GWP 20 years	GWP 100 years
Carbon dioxide	CO_2	Variable	1	1
Methane	CH_4	12.4	84	28
Nitrous oxide	N_2O	121	264	265
Tetrafluoromethane	CF_4	**50000**	**4880**	**6630**
Hexafluoroethane	C_2F_6	**10000**	**8210**	**11100**

GWP: Global Warming Potential

Primary Aluminium production and PFCs emissions

- When the **alumina** ore content of the electrolytic bath **falls** below **critical levels** required for electrolysis, rapid **voltage increases** occur, termed "**anode effects**".
- Anode effects cause carbon from the anode and fluorine from the dissociated molten cryolite bath to combine, producing CF_4 and C_2F_6 due to the following reactions:

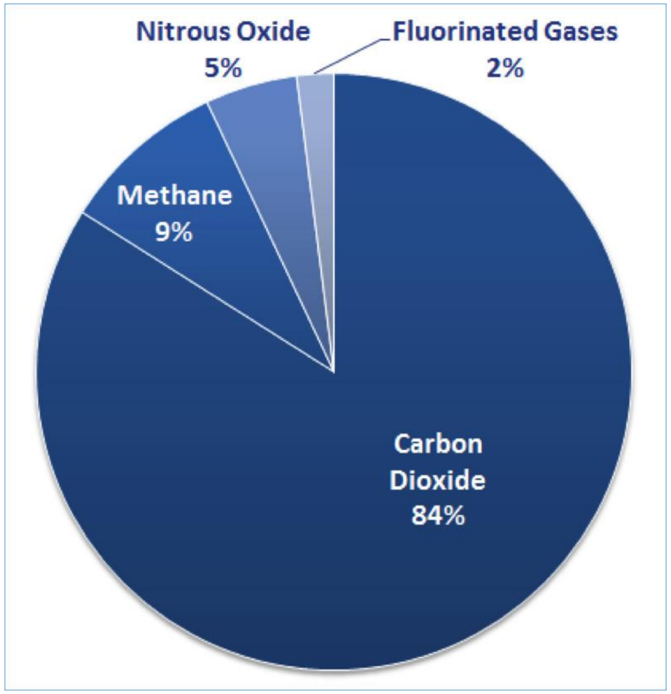
$$\mathbf{Na_3AlF_6 + \tfrac{3}{4}\,C \rightarrow Al + 3NaF + \tfrac{3}{4}\,CF_4}$$

$$\mathbf{Na_3AlF_6 + C \rightarrow Al + 3NaF + \tfrac{1}{2}\,C_2F_6}$$

- The primary PFC emissions pathway is the exhaust duct collection system, which removes gases from the pots.

Primary Aluminium production and PFCs emissions

- The frequency and duration of **anode effects** depend primarily on the pot **technology** and operating **procedures**.
- Emissions of **CF_4** and **C_2F_6**, therefore, **vary** significantly from one aluminium smelter to another **depending** on several factors.
- The factors that can potentially influence the PFC generation rate are:
  - Cell Technology Type
  - Feed Delivery System
  - Cell Operating Parameters
  - Anode Effect Kill Routine
  - Electrolyte Properties
  - Cell Liquid Velocities
  - Alumina Quality
  - Anode Coke
  - Smelter Configuration



Primary Aluminium production and PFCs emissions

- The **methods**, assumptions, and **data** used to estimate PFCs emissions from primary aluminium production are **not clear**, not transparent or **not well documented**.
- **Lack** of transparency in reporting **makes impossible** to review, compare, or **verify emission** estimates.
- It is possible to develop a **smelter-specific relationship** between emissions and potentially relevant operating parameters.
- **PFC emissions** from primary aluminium production should be calculated on **a smelter basis**.

Primary Aluminium production and PFCs emissions

- **Perfluorocarbons** (PFCs) are **greenhouse** gases with atmospheric **lifetimes** of more than **1000 years**.
- **PFCs** have greenhouse effects **6,500 to 9,200** than **CO_2**. Even there **mixing ratios** are very small (**ppb** and **ppt** levels in air), they are **highly effective** greenhouse gases.
- They are **powerful greenhouse** gases and today's **emissions** will still be affecting earth's **climate** in the **next millennium**.
- The only known **sinks** for these greenhouse gases are l**ight destruction** (photolysis) or **ion reactions** in our **mesosphere**.
- A new and **worrying development** has been the **discovery** of a **hybrid greenhouse gas** derived from PFCs and SF_6 (**SF_5CF_3**).
- **SF_5CF_3** is the **most powerful** greenhouse gas discovered and whose **concentration** is **rising** rapidly.

Monitoring and control of PFCs emission

- The good **practice** method requires developing or choosing a **smelter-specific** relationship between PFCs emissions and relevant operating parameters.
- In order to develop the **relationship** between emissions and process parameters, operational data must be compiled simultaneously with the **emissions measurements**.
- To demonstrate the applicability of **an estimation model**, emissions must be measured in **the smelters** at least once to **ensure** the applicability of the **model**.

Monitoring and control of PFCs emission

- The **choice** of sampling **method**, sampling **scale**, and **analytical** methods is **critical in developing** a robust relationship.
- **Analytical system** must be appropriate for the sampling method, stable, and **free of** (or corrected for) **interferences**.
- The **detection limits** of the analytical system must be **sufficient** to detect **PFCs concentrations** in the exhaust duct and potroom roofs.
- **Gas chromatography** is a selective method for qualifying and quantifying PFCs.

Monitoring and control of PFCs emission

- The lowest **detection** limit for PFCs are obtained with **FTIR analysis** performed within particular conditions.
- Detection limits of **0.7 ppbv** for CF_4 and **1.1 ppbv** for C_2F_6 were measured with a 10-meter path length gas cell.
- The sampling can be done by using **gas bag** or **canister**.
- The lifetime of a sample is about 48 hours for a **gas bag** and 30 days for a **canister**.
- Use of thermal desorption of **PFCs** is a novel approach for the characterization of **fugitive** and duct **exhaust emissions** from primary aluminum smelters.

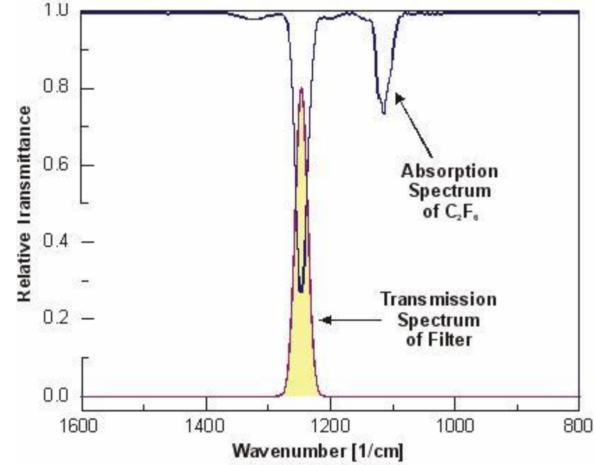


Figure 1: Detection priciple of an NDIR photometer.

Passive Absorber For sampling

The detection limit and uncertainty:
LOD is 7 $\mu g/m^3$ for 24 hours exposure
The uncertainty at 2σ is 4.5 % over the whole exposure range.

Online monitoring

Continuous measurements using Lasers

- Lasers for HF and Dust already commercially available
- Continues measure of air flow, either through ultrasonic or by laser
- PFC laser system coming up and will become a good alternative

Conclusions

- Today's sampling standards are being challenged by both need for accuracy (reduced levels, detection limits) and the future need for same time information.
- The future emission control will trend towards online monitoring.
- Long term sampling using passive absorbers can be utilized as "manual" verification of online systems
- The demand for PFC control will demand development both on sampling techniques and online systems, absorbers would ease the sampling
- Environmental data's must become a part of the operational parameters, and not only a reporting value
- Online monitoring includes emission values into process variables and can both save environment but also preserve value

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Thank you for your attention