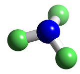

What is Nitrogen trifluoride (NF_3)?

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Nitrogen trifluoride (NF_3) is a synthetic inorganic chemical. It is manufactured by the reaction of hydrochloric acid (HCl) and ammonia (NH_3). It is toxic, odorless, colorless, non-flammable, and is an oxidizing gaseous substance at room temperature and atmospheric pressure[1]. Once NF_3 is released into the atmosphere, it circulates from the surface to the stratosphere hundreds of times before it is destroyed by solar ultraviolet radiation. It is nearly chemically inert in the atmosphere, and **the average lifetime of an NF_3 molecule in the atmosphere is about 550 years**[2], far beyond a human lifespan.

NF_3 is very effective in absorbing the infrared radiation that the Earth emits. By trapping this infrared radiation, NF_3 becomes a potent greenhouse gas. The **Global warming potential** (**GWP**), defined as a multiple of the heat that would be absorbed by the same mass of carbon dioxide (CO_2) tells us the heat absorbed by any greenhouse gas in the atmosphere compared with CO_2 (by definition GWP is 1 for CO_2). The GWPs of NF3 are 16,800, 12,200 and 18,700 for time horizons of 20-, 100-, and 500-years, respectively[2]. These values mean that NF_3 is 16,800, 12,200 and 18,700 times more powerful than CO_2 in trapping atmospheric heat over a 20-, 100-, and 500-year timespan, respectively.

The increasing GWP with time horizon reflects the longer atmospheric residence time of NF_3 compared with that of CO_2. In fact, compared to the original 6 Kyoto-listed gases, the GWP of NF3 is second only to that of SF_6 (100-yr GWP = 22,800). On a per molecule basis, the radiative efficiency of NF_3 is high, 0.21 $W\ m^{-2}$ per ppb [3], placing near the top of the low-molecular weight HFCs and between CF_4 (0.10) and C_2F_6 (0.26).

According to the United Nations Framework Convention on Climate Change (UNFCCC), manufacturers use NF_3 as a "chamber-cleaning gas" in production processes to clean unwanted buildups on microprocessor and circuit parts as they are being constructed. A gas called hexafluoroethane (C_2F_6), which the first Kyoto compliance period did regulate, used to corner this market, but NF_3 became a strong competitor due to its lower costs and its initial absence from the Kyoto Protocol. NF_3 'has a greater impact on Earth's climate per unit mass of emissions' than the C_2F_6 that it replaced.

Industrial Applications and Increasing Demand

NF3 offers a number of advantages of relative ease of use at ambient conditions that have made it very popular in industrial applications: it is non-corrosive, non-reactive, and easy to manage chemical and reactivity hazards during storage, transportation, and normal operations. It has the ability to act as a stable fluorinating agent and has a wide application scope in high-energy laser at dry etching in semiconductor production as a filling gas in lamps to prolong their durability and increase brightness, as well as a detergent gas in CVD apparatus. For all these reasons, nitrogen trifluoride is increasingly used in the electronics industry, primarily for the etching of microcircuits, and for manufacturing of liquid crystal flat panel displays and thin film PV cells.

The robust development of the consumer electronics market has produced a tremendous growth in the global nitrogen trifluoride market in the last years. In addition, due to the rising demand for flat panel displays, LCD televisions and several other electronic products, the market for NF_3 has exploded across the globe. The rising disposable income of consumers and their improving lifestyle, especially in developing economies are further estimated to accelerate the growth of the global market in the coming years. In fact, NF3 production has consequently increased 15%–17% a year, from 1,000 tons (1 Ton = 10^6 grams) produced in 1992 to more than 28.5 kTons (1kTon = 10^9 g) in 2019 (see Table 1 for the values in 2019). Figure 1 shows the NF3 market volume in North America since 2012, and the current projection values for 2024, after Expert Market Research (https://www.expertmarketresearch.com/).

Region	Total emissions of NF3	% of worldwide market
Asia	25.20 kTons	88.0%
North America	2.40 kTons	8.5%
Europe	1.03 kTons	3.5%
Total	**28.63 kTons**	

Table 1. NF_3 total emissions and % of the worldwide market in 2019.

Asia is currently the largest regional NF3 market. The growth of the semiconductor industry in South Korea, China, and Japan is expected to drive augmented NF3 market demand in the production of semiconductors. Demand is expected to be further propelled owing to increasing desire for flat panel displays in emerging markets such as China and India. In Europe, the increase in the government regulations to support the semiconductor and electronics industry to compete in the Asia Pacific and North American markets and to promote economic growth in the region is projected to have a positive impact on the market growth.

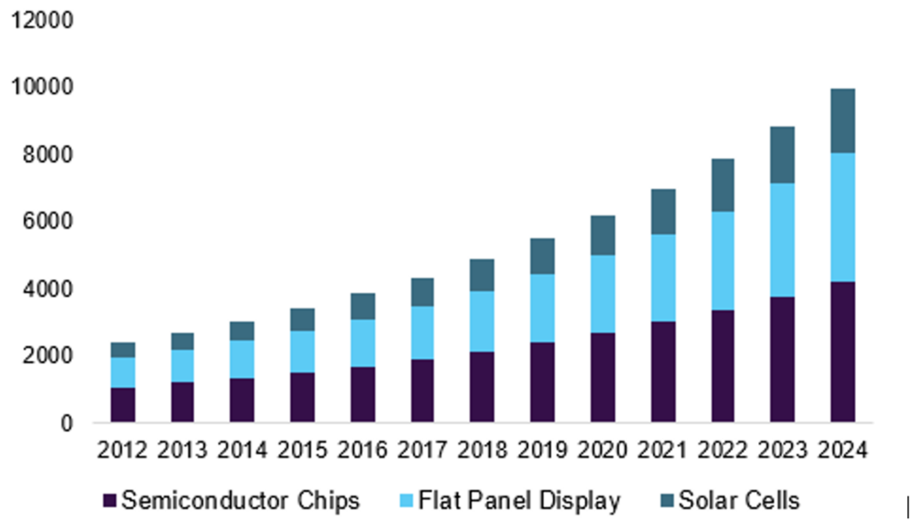

Fig. 1. NF3 market volume in North America since 2012. At the current growing rate, the market will increase 53% by 2024 from today´s numbers, after Expert Market Research (https://www.expertmarketresearch.com/).

Control of NF3 emissions and legislation

According to Robson et al.[3] , most of NF_3 is used in a manner such that only 2% escapes to the atmosphere. Based on that study, the major NF3 producers assess that 98% of the gas is destroyed during the manufacturing process, and thus NF3 is an environmentally safe gas. **However, there should be no doubt that NF3 is a highly hazardous gas in terms of global warming**. We have no reliable estimates about leakage during production, shipping and decommission. This gas is extremely volatile and difficult to measure at low abundances, so we cannot be sure that industry estimates or measurements are accurate.

Moreover, studies by Lee et al·[4] show a maximum destruction efficiency of less than 97% under ideal conditions; and there is an economic incentive, a tradeoff between more efficient NF_3 destruction and faster throughput[5], which encourages greater emissions. These emission fractions for NF_3 do not include fugitive release during its manufacture, transport, application, or disposal.

Experience with the ozone-depleting gas CFC-12[6], has shown that emission inventories from the chemical industry cannot be relied upon. **Once released to the atmosphere, gases like CFC-12 and NF_3 will take centuries to clean out**. Given this potential, the production of high-GWP, long-lived, greenhouse gases like NF_3 should be included in the national greenhouse gas inventories once global usage exceeds a threshold, e.g., 5 $MMTCO_2$, no matter what the claim for containment.

Returning to the intent of UNFCCC Article 3.3 (''policies and measures should... cover all relevant sources, sinks and reservoirs of green- house gases ...''), it seems prudent to expand the list of greenhouse gases to include NF3 emissions. Total NF3 emissions are significantly larger than expected assuming global implementation of ideal industrial practices. As such, there is a need for improvements in NF3 emissions reduction strategies to keep pace with its increasing use and to slow its rising contribution to anthropogenic climate forcing.

NF3 is a gas of purely anthropogenic origin that has three important properties that make it a dangerous enemy: it has a large global warming potential, due to its 500 years lifetime it is accumulating in the Earth's atmosphere, and its rapid rise in production by the chemical industry has gone almost unnoticed. NF_3 has a potential greenhouse impact larger than that of the industrialized nations' emissions of PFCs or SF_6, or even that of the world's largest coal-fired power plants. Although the instantaneous radiative forcing due to NF3 is currently small, its atmospheric lifetime essentially makes emissions cumulative with an effect lasting beyond usual societal timescales.

References

1. National Center for Biotechnology Information (2020). PubChem Compound Summary for CID 24553, Nitrogen trifluoride. Retrieved October 15, 2020 from https://pubchem.ncbi.nlm.nih.gov/compound/Nitrogen-trifluoride.
2. **Prather and Hsu (2008)**, NF_3, the greenhouse gas missing from Kyoto, Geophysical Research Letters, VOL. 35, L12810, doi:10.1029/2008GL034542.
3. **Robson, J. I., et al. (2006**), Revised IR spectrum, radiative efficiency and global warming potential of nitrogen trifluoride, *Geophys. Res. Lett.*, *33*, L10817, doi:10.1029/2006GL026210.
4. **Lee, J.-Y., et al. (2007),** Evaluation method on destruction and removal efficiency of perfluorocompounds from semiconductor and display, *Bull. Korean Chem. Soc.*, *28*, 1383 – 1388.
5. **Pruette, L., et al. (1999),** Evaluation of a dilute nitrogen trifluoride plasmaclean in a dielectric PECVD reactor, Electrochem. Solid State Lett., 2(11),592–594.
6. **Rowland, F. S. et al.** (1982), Dichlorodifluoromethane, CCl_2F_2, in the Earth's atmosphere, *Geophys. Res. Lett.*, *9*, 481 – 484.