

**TECHNICAL SUPPORT DOCUMENT FOR
INDUSTRIAL GAS SUPPLY: PRODUCTION,
TRANSFORMATION, AND DESTRUCTION OF
FLUORINATED GHGS AND N₂O**

**PROPOSED RULE FOR MANDATORY
REPORTING OF GREENHOUSE GASES**

Office of Air and Radiation
U.S. Environmental Protection Agency

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1. Source Description

Fluorinated greenhouse gases (fluorinated GHGs) are man-made gases used in several sectors. They include hydrofluorocarbons (HFCs), perfluorocarbons (PFCs), sulfur hexafluoride (SF₆), nitrogen trifluoride (NF₃), and a number of fluorinated ethers. (Fluorinated GHGs also include chlorofluorocarbons (CFCs) and hydrochlorofluorocarbons (HCFCs), but these ozone-depleting substances (ODSs) are currently being phased out and otherwise regulated under the Montreal Protocol and Title VI of the Clean Air Act, and EPA is not proposing requirements for them under the GHG Reporting rule.) Hydrofluorocarbons (HFCs) are the most commonly used fluorinated GHGs, used primarily to replace ozone-depleting substances in a number of applications, including air-conditioning and refrigeration, foams, solvents, and aerosols. PFCs are used in fire fighting and to manufacture semiconductors and other electronics. Sulfur hexafluoride (SF₆) is used in a diverse array of applications, including electrical transmission and distribution equipment (as an electrical insulator and arc quencher) and in magnesium casting operations (as a cover gas to prevent oxidation of molten metal). Nitrogen trifluoride (NF₃) is used in the semiconductor industry, increasingly to reduce overall semiconductor greenhouse gas emissions through processes such as NF₃ remote cleaning and NF₃ substitution during in-situ cleaning. Fluorinated ethers (HFEs and HCFEs) are used as anesthetics (e.g., isoflurane, desflurane, and sevoflurane) and as heat transfer fluids (e.g., the H-Galdens). The ability of fluorinated GHGs to trap heat in the atmosphere is often thousands to tens of thousands as great as that of CO₂, on a pound-for-pound basis. Some fluorinated GHGs are also very long lived; SF₆ and the PFCs have lifetimes ranging from 3,200 to 50,000 years (IPCC, 2006).

Once produced, fluorinated GHGs can have hundreds of millions of downstream emission points. For example, the gases are used in almost all car air-conditioners and household refrigerators and in other ubiquitous products and applications. Thus, tracking emissions of these gases from downstream uses would be extremely difficult.

In addition, fluorinated GHGs may also be used as feedstocks to produce other chemicals. Conversations with chemical manufacturers indicate that there is at least one case in which an HFC is used as a feedstock, and that use of HFCs as feedstocks is likely to grow. There are numerous examples of CFCs being used as feedstocks, including the use of CFC-113a to manufacture HFC-134a and HFC-245fa and the use of CFC-114 to manufacture a series of vinylidene compounds used in various products and applications. Although CFCs are excluded from the definition of fluorinated GHG, they are in some ways chemically similar to HFCs.

Nitrous oxide (N₂O), a clear, colorless, oxidizing gas with a slightly sweet odor is produced primarily for use in carrier gases with oxygen to administer more potent inhalation anesthetics for general anesthesia and as an anesthetic in various dental and veterinary applications. N₂O is a strong greenhouse gas with a global warming potential of 310 (SAR).

The reporting of fluorinated GHG emissions from the production process is addressed in a separate technical support document (EPA-HQ-OAR-2008-0508-012).

a. Total U.S. Production

In 2006, 23 U.S. facilities produced over 350 million mtCO₂e of HFCs, PFCs, SF₆, fluorinated ethers, N₂O, and NF₃. More specifically, 2006 production of HFCs is estimated to have

exceeded 250 million mtCO₂e while production of PFCs, SF₆, fluorinated ethers, N₂O, and NF₃ is estimated to have been near 150 million mtCO₂e. The quantities of HFCs, PFCs, SF₆, fluorinated ethers, N₂O, and NF₃ transformed and destroyed are currently unknown.

For some of the GHGs listed above, including fluorinated ethers and NF₃, the IPCC Second Assessment Report (SAR) does not provide GWPs. Table 1 presents recent GWPs for several fluorinated ethers, including H-Galdens and anesthetics such as desflurane (HFE-236ea2) and isoflurane (HCFE-235da2).

Table 1. GWPs for Selected GHGs from AR-4, the 2006 Scientific Assessment of Ozone Depletion, and TAR

Name	#	CAS #	Chemical Formula	Global Warming Potential (100 yr.)		
				IPCC Fourth Assessment Report	WMO Scientific Assessment of Ozone Depletion	IPCC Third Assessment Report
HFE-125	125	3822-68-2	CHF ₂ OCF ₃	14,900	14,910	14,900
HFE-134	134	1691-17-4	CHF ₂ OCHF ₂	6,320	6,320	6,100
HFE-143a	143a	421-14-7	CH ₃ OCF ₃	756	756	750
HFE-227ea	227ea	2356-62-9	CF ₃ CHFOCF ₃	1,540 ^a	1,540	1500
Isoflurane	235da2	26675-46-7	CHF ₂ OCHClCF ₃	350	349	340
HG-10	236ca12	Not available	CHF ₂ OCF ₂ OCHF ₂	2,800	2,820	2,700
Desflurane	236ea2	57041-67-5	CHF ₂ OCHF ₂ CF ₃	989 ^a	989	960
HFE-236fa	236fa	20193-67-3	CF ₃ CH ₂ OCF ₃	487 ^a	487	470
HFE-245cb2	245cb2	22410-44-2	CH ₃ OCF ₂ CF ₃	708 ^a	708	Not listed
HFE-245fa1	245fa1	Not available	CHF ₂ CH ₂ OCF ₃	286 ^a	286	280
HFE-245fa2	245fa2	1885-48-9	CHF ₂ OCH ₂ CF ₃	659	659	570
HFE-254cb2	254cb2	425-88-7	CH ₃ OCF ₂ CHF ₂	359	359	30
HFE-263fb2	263fb2	460-43-5	CF ₃ CH ₂ OCH ₃	11 ^a	Not listed	11
HFE-329mcc2	329mcc2	67490-36-2	CF ₃ CF ₂ OCF ₂ CHF ₂	919 ^a	919	890
HFE-338mcf2	338mcf2	156-05-3	CF ₃ CF ₂ OCH ₂ CF ₃	552 ^a	552	540
HG-01	338pcc13	Not available	CHF ₂ OCF ₂ CF ₂ OCHF ₂	1,500	1,500	1,500
HFE-347mcc3	347mcc3	28523-86-6	CH ₃ OCF ₂ CF ₂ CF ₃	575	575	480
HFE-347mcf2	347mcf2	Not available	CF ₃ CF ₂ OCH ₂ CHF ₂	374 ^a	374	360
HFE-347pcf2	347pcf2	406-78-0	CHF ₂ CF ₂ OCH ₂ CF ₃	580	Not listed	Not listed
HFE-356mec3	356mec3	382-34-3	CH ₃ OCF ₂ CHFCF ₃	101 ^a	101	98
HFE-356pcc3	356pcc3	Not available	CH ₃ OCF ₂ CF ₂ CHF ₂	110	110	110
HFE-356pcf2	356pcf2	Not available	CHF ₂ CH ₂ OCF ₂ CHF ₂	265 ^a	265	260
HFE-356pcf3	356pcf3	35042-99-0	CHF ₂ OCH ₂ CF ₂ CHF ₂	502 ^a	502	430
HFE-365mcf3	365mcf3		CF ₃ CF ₂ CH ₂ OCH ₃	11 ^a	Not listed	11
HFE-374pc2	374pc2	512-51-6	CH ₃ CH ₂ OCF ₂ CHF ₂	557 ^a	557	540
N/A	N/A	13171-18-1	(CF ₃) ₂ CHOCH ₃	27	Not listed	26

N/A	N/A	Not available	$\text{CH}_3\text{OCF}(\text{CF}_3)_2$	343 ^a	343	330
N/A	N/A	Not available	$(\text{CF}_3)_2\text{CHOH}$	195	217	190
N/A	N/A	Not available	$\text{CF}_3\text{CF}_2\text{CH}_2\text{OH}$	42	Not listed	40
N/A	N/A	26103-08-2	$\text{CHF}_2\text{OCH}(\text{CF}_3)_2$	380 ^a	379	370
N/A	N/A	Not available	$-(\text{CF}_2)_4\text{CH}(\text{OH})-$	73 ^a	72	70
H-Galden 1040x	43-10pccc124	Not available	$\text{CHF}_2\text{OCF}_2\text{OC}_2\text{F}_4\text{OCHF}_2$	1,870	1,870	1,800
Novac HFE-7100	449sl	163702-07-6	$\text{C}_4\text{F}_9\text{OCH}_3$			
		163702-08-7 ^b	$(\text{CF}_3)_2\text{CFCF}_2\text{OCH}_3^b$	297	404	390
Novac HFE-7200	569sf2	163702-05-4	$\text{C}_4\text{F}_9\text{OC}_2\text{H}_5$			
		163702-06-5 ^b	$(\text{CF}_3)_2\text{CFCF}_2\text{OC}_2\text{H}_5^b$	59	57	55
PFPME	Not available	Not available	$\text{CF}_3\text{OCF}(\text{CF}_3)\text{CF}_2\text{OCF}_2\text{OCF}_3$	10,300	Not listed	Not listed
Nitrogen Trifluoride	Not available	7783-54-2	NF_3	17,200	18,000	10,800
Trifluoromethyl sulfur pentafluoride			SF_5CF_3	17,700	17,960	>17,500

^aListed in errata sheet updated 31 July 2008.

^bInseparable isomer.

N/A = not applicable. These chemicals fall outside of the typical HFE naming convention.

GWPs listed in italics under the Third Assessment Report were determined indirectly rather than through laboratory measurements.

The GWP for sevoflurane, a common anesthetic, has not been published in any IPCC or WMO Assessment. However, one study estimated that the absolute GWP for sevoflurane at an infinite time horizon was two percent of the absolute direct GWP of CFC-12 at an infinite time horizon (Langbein, 1999). Adjusting this value to a 100-year time horizon and multiplying it by the 100-year direct GWP given for CFC-12 in AR-4 provides a 100-year GWP for sevoflurane of 345.

2. Options for the Scope of Activities Reported

Because fluorinated GHGs and N_2O have an extremely large number of relatively small downstream sources, reporting of downstream emissions of these gases would be incomplete, impractical, or both. On the other hand, the number of upstream producers, importers, and exporters is comparatively small, and the quantities that would be reported by individual gas suppliers are often quite large. Thus, upstream reporting is likely to be far more complete and cost-effective than downstream reporting.

Downstream emissions are most closely related to the upstream quantity known as “consumption,” which is defined as the sum of the quantities of chemical produced in or imported into the United States minus the sum of the quantities of chemical transformed (used as a feedstock in the production of other chemicals), destroyed, or exported from the United States. (Chemical that is exported, transformed, or destroyed will never be emitted in the United States.) EPA reviewed a number of protocols that track chemical consumption, its components (production, import, export, etc.), or similar quantities. These protocols included EPA’s Stratospheric Ozone Protection regulations at 40 CFR Part 82, the Australian Commonwealth

Government Ozone Protection and Synthetic Greenhouse Gas Reporting Program, the EU Regulation on Certain Fluorinated Greenhouse Gases (No. 842/2006), EPA’s Chemical Substances Inventory Update Rule at 40 CFR 710.43, EPA’s Acid Rain regulations at 40 CFR Part 75, the Toxic Release Inventory (TRI) Program, and the 2006 IPCC Guidelines.

EPA reviewed these protocols both for their overall scope and for their specific requirements for monitoring and reporting. The monitoring requirements for production, transformation, and destruction are discussed in section 4 below. (The monitoring requirements for imports and exports are discussed in separate technical support documents.)

Four of these protocols are designed specifically to monitor the supply of a set of chemicals within a country. These include EPA’s Stratospheric Protection Program, the EU Regulation on Certain Fluorinated Greenhouse Gases, the Australian Synthetic Greenhouse Gas Reporting Program, and EPA’s Chemical Substances Inventory Update Rule. All four of these programs require reporting of production and imports, and the first three also require reporting of exports. In addition, the EU regulation and EPA’s Stratospheric Ozone Protection Program require reporting of the quantities of chemicals transformed or destroyed. By accounting for all chemical flows into and out of their respective jurisdictions, including destruction and transformation, these two programs result in estimates of consumption that are more closely related to actual country/regional emissions than are estimates of consumption that do not account for all of these flows.

3. Options for Reporting Threshold

EPA evaluated a range of threshold options for facilities producing fluorinated GHGs and N₂O. These included production-based thresholds of 1,000, 10,000, 25,000 and 100,000 mtCO₂e and capacity-based thresholds equivalent to these. EPA also evaluated a requirement that all production facilities be required to report.

The capacity thresholds were developed based on full capacity utilization. This is a somewhat conservative assumption since capacity utilization is often below 100 percent, but production can fluctuate, and this assumption ensures that facilities that have a reasonable chance of producing more than the threshold quantity.

Table 2 below shows the emissions and facilities that would be covered under the various thresholds for production and bulk imports of N₂O and HFCs, PFCs, SF₆, and NF₃.

Table 2: Threshold Analysis for Industrial Gas Supply

Source Category	Emission Threshold Level ²	Total National Production or Import (mtCO ₂ e)	Number of Facilities	Production or Imports Covered		Facilities Covered	
				mtCO ₂ e/yr	Percent	Number	Percent
HFC, PFC, SF ₆ , and NF ₃ Producers	1,000	350,000,000	12	350,000,000	100%	12	100%
	10,000	350,000,000	12	350,000,000	100%	12	100%
	25,000	350,000,000	12	350,000,000	100%	12	100%
	100,000	350,000,000	12	350,000,000	100%	12	100%

Source Category	Emission Threshold Level ²	Total National Production or Import (mtCO ₂ e)	Number of Facilities	Production or Imports Covered		Facilities Covered	
				mtCO ₂ e/yr	Percent	Number	Percent
N₂O Producers	1,000	4,500,000	5	4,500,000	100%	5	100%
	10,000	4,500,000	5	4,500,000	100%	5	100%
	25,000	4,500,000	5	4,500,000	100%	5	100%
	100,000	4,500,000	5	4,500,000	100%	5	100%
N₂O and Fluorinated GHG Importers (bulk)	1,000	110,024,979	116	110,024,987	100%	111	96%
	10,000	110,024,979	116	109,921,970	99.9%	81	70%
	25,000	110,024,979	116	109,580,067	99.6%	61	53%
	100,000	110,024,979	116	108,703,112	98.8%	44	38%

As can be seen from Table 2, all identified N₂O and HFC, PFC, SF₆, and NF₃ production facilities would be covered at all capacity and production-based thresholds considered in this analysis.

EPA does not have facility-specific production capacity information for the six facilities producing fluorinated anesthetics; however, if total estimated U.S. production were evenly divided among these six facilities, they too would be covered at all capacity and production-based thresholds.

Either a capacity-based threshold or a requirement that all facilities report would permit facilities to quickly determine whether or not they must report under this rule. The one potential drawback of requiring reporting for all production facilities is that small-scale production facilities (e.g., for research and development) could be inadvertently required to report their production, even though the quantities produced would be small in both absolute and CO₂-weighted terms.

EPA also considered a range of publications from which to draw the 100-year GWPs that producers would use to determine whether their CO₂-equivalent production exceeded the applicable threshold. These included the IPCC Second Assessment Report (SAR) and later IPCC and other reports (e.g., the 2006 Scientific Assessment of Ozone Depletion published by the World Meteorological Organization.) The advantage of using the GWPs published in the SAR is that these are the GWPs that are used for current U.S. and international reporting of CO₂-equivalent GHG emissions. The disadvantage is that the SAR does not list GWPs for some of the fluorinated GHGs that are coming into increasing use (notably NF₃ and many of the fluorinated ethers). However, if SAR GWPs were not available, importers could use the most recent GWP from either an IPCC Assessment Report or a WMO Scientific Assessment of Ozone Depletion.

4. Monitoring Methods and Current Plant Practices

a. Production

In developing the proposed rule, EPA reviewed a number of protocols for estimating production and other flows. These include the *2006 IPCC Guidelines*, Title VI of the Clean Air Act (CAA), Part 75 Appendix D (measurement requirements for oil and natural gas), the Toxic Release Inventory (TRI), the Technical Guidelines for the Voluntary Reporting of Greenhouse Gases (1605(b)) Program, the Toxic Substances Control Act (TSCA) Chemical Substance Inventory, EPA's Climate Leaders Program, The Climate Registry, the EU Regulation on Certain Fluorinated Greenhouse Gases (No. 842/2006), and the EU's Article 6 reporting. As discussed below, EPA also reviewed the methods currently used by production facilities to measure their production.

The accuracy and precision of measurements of production are determined by (1) the accuracy and precision of the instruments used to measure production, and (2) the completeness with which the various flows of product into and out of the production process are characterized. The methods described in the protocols and guidance differ in their level of specificity regarding their precision and accuracy requirements. Some programs, such as Title VI, TSCA, and EC's Article 6 do not specify any accuracy requirement, while other programs specifically define acceptable errors and reference industry standards for calibrating and verifying monitoring equipment. One of the latter is Part 75, Appendix D, which establishes requirements for measuring oil and gas flows as a means of estimating SO₂ emissions from their combustion.

The high GWPs and large volumes of fluorinated GHGs produced make precise measurements important for this source category. For example, a one-percent error at a typical facility producing fluorinated GHGs would equate to 300,000 mtCO₂e. Even a 0.2 percent error equates to 60,000 mtCO₂e, but 0.2 percent is near the precision limit of modern flowmeters, making greater precision difficult. Moreover, as is discussed in the Technical Support Document for Emissions from Production of Fluorinated GHGs (EPA-HQ-OAR-2008-0508-012), the precision of the production measurement (as well as of the reactant and byproduct measurements) strongly affects the precision of the estimate of emissions from the production process when the mass-balance approach is used. EPA believes that requirements for precise and accurate measurements (e.g., precisions and accuracies of 0.2 percent) should not represent a significant burden to chemical producers, who already use and regularly calibrate measurement devices with similar accuracies and precisions.

Measuring devices could be positioned wherever production of the facility is traditionally measured, e.g., at the inlet to the day tank or at the shipping dock.

In some cases, production facilities accept used GHG product for reclamation and add this product back into the production process. To avoid counting this used GHG product as new production, owners or operators of facilities that produce N₂O or fluorinated GHGs could be required to measure any quantities of these GHGs that they add to the production process upstream of the production measurement. These quantities would be subtracted from the total mass of product measured at the end of the process.

b. Destruction

In its evaluation of options for monitoring and reporting destruction of fluorinated GHGs, EPA took into consideration the existing reporting requirements for ODS destruction under EPA's Stratospheric Ozone Protection program and the proposed reporting requirements for HFC-23 destruction from the production of HCFC-22 (see Technical Support Document EPA-HQ-OAR-2008-0508-015). A brief description of each follows. EPA also considered issues that arise in the destruction of SF₆ and PFCs, which are relatively difficult to destroy.

Reporting of ODS Destruction and Transformation

Under the Stratospheric Ozone Protection Program, ODS to be destroyed or transformed can, in some cases, be imported or produced without expending production or consumption allowances. In these cases, producers and importers of ODS are required to report and document the amount and type of ODS that they destroy or transform or that they sell or transfer to another company for destruction or transformation. In addition, persons destroying or transforming ODS are required to provide verification of destruction or transformation to producers and importers and to EPA.

Where controlled ODS were originally produced without expending allowances, persons who purchase or otherwise receive ODS from a producer or importer of ODS and subsequently destroy the ODS are required to provide a destruction verification document to the producer or importer. This verification document must include:

- the identity and address of the person intending to destroy controlled substances;
- an indication of whether those controlled substances will be “completely destroyed” or less than completely destroyed, in which case the person must provide the DE;¹
- the period of time over which the person intends to destroy the controlled substances; and
- the signature of the verifying person.

A revised copy of the verification must be submitted to the producer or importer if any aspects of the verification change.

Similarly, persons who purchase ODS from a producer or importer and who subsequently transform the ODS are required to provide the producer or importer with the IRS certification that the controlled substances will be transformed.

The producer or importer must submit a copy of the destruction verification or transformation certification to EPA along with the names and quantities of all ODS destroyed during a control period and a copy of the invoice or receipt documenting the sale of the controlled substance. This receipt must include the name, address, contact person and telephone number of the transformer or destroyer.

Additionally, those persons who destroy or transform ODS and who submitted a destruction verification or an IRS certificate of intent to transform to a producer and/or importer are required to report to EPA the names and quantities of ODS destroyed or transformed during the control period (i.e. one calendar year).

¹ “Completely destroy,” as defined in 40 CFR Part 82.3, Subpart A, means “to cause the expiration of a controlled substance at a destruction efficiency of 98 percent or greater, using one of the destruction technologies approved by the Parties.”

In addition to these periodic reports, persons who destroy ODS must submit to EPA a one-time report detailing:

- the destruction unit's destruction efficiency,
- the methods used to record the volume destroyed,
- the methods used to record destruction efficiency, and
- the names of other relevant Federal or State regulations that may apply to the destruction process.

If there are changes in a facility's destruction efficiency (DE) and/or methods used to record the volume destroyed or used to determine DE, the facility must submit a revised report to EPA within 60 days of the change.

Practice and Efficiency of ODS Destruction

Under the Stratospheric Ozone Protection Program, "destruction" is defined as the expiration of a controlled substance (ODS) to the destruction efficiency actually achieved, using one of six processes approved by the Parties to the Montreal Protocol.

Most facilities that destroy ODS in the United States are permitted hazardous waste combustors (HWCs). U.S.-based HWCs are highly regulated entities, subject to regulation under both the Clean Air Act (CAA) and RCRA, as well as associated state statutes and regulations. Further, HWCs have been subjected to site-specific risk assessments (SSRAs) on a facility-specific basis to ensure that air emissions from those facilities do not pose unacceptable risks to human health and the environment, and any such risks identified are subject to and mitigated by risk-based RCRA permit limits established by the permitting agency (EPA, 2007).

Facilities destroying ODS that are considered RCRA hazardous waste (specifically, some CFCs, methyl chloroform, carbon tetrachloride, and methyl bromide) are required to meet the applicable Maximum Achievable Control Technology (MACT) standards for HWCs, which include the minimum destruction and removal efficiency (DRE) of 99.99 percent for RCRA hazardous wastes. Performance testing is most often not conducted using ODS, but rather, using a few representative compounds that are more difficult to destroy than ODS. Conducting performance testing using ODS is possible, but would impose additional costs on facilities that would vary depending on whether the test was conducted in conjunction with an already scheduled performance test (EPA, 2007).

It is likely that this minimum required DRE is also being met for other ODS *not* listed as RCRA hazardous wastes that are destroyed by RCRA-permitted HWCs, based on their test protocols, permitting requirements and actual performance data. HWCs typically operate at temperatures above 1800°F, which are believed to be sufficient to destroy CFCs, HCFCs, and halons (EPA, 2007).

Proposed Reporting of HFC-23 Destruction

EPA is also considering requiring reporting of HFC-23 destruction as explained in the document, "Technical Support Document for Emissions of HFC-23 from the Production of HCFC-22" (EPA-HQ-OAR-2008-0508-015). Verifying the performance of the destruction device is important because if the destruction device malfunctioned, were not operated properly, or were unused for some other reason, emissions of HFC-23 from each of the U.S. HCFC-22 production

plants could easily exceed all thresholds for this source category. HFC-23 destruction facilities could be required to perform annual HFC-23 concentration measurements by gas chromatography to confirm that emissions from the destruction device are as low as expected based on the rated DE of the device. Although the initial testing and parametric monitoring that facilities currently perform on their destruction device provides general assurance that the device is performing correctly, an annual measurement would provide additional assurance at relatively low cost (e.g., approximately two hours of technician time per year to sample and analyze the vent gases). Even a one- or two-percent decline in the average destruction efficiency of destruction devices could lead to emissions of more than 100,000 mtCO₂e, making this a particularly important factor to monitor accurately.

Currently, two of the three operating HCFC-22 production facilities either destroy the HFC-23 that they generate or recapture it for destruction elsewhere. The facility that destroys the HFC-23 on site uses a thermal oxidizer that operates at temperatures above 2,300 degrees F. In 1994, the inlet and outlet of this thermal oxidizer were both sampled to determine the DE for HFC-23, which was measured as greater than 99.996 percent. The facility that recaptures the HFC-23 for destruction elsewhere (another facility owned by the same company) reports that the thermal converter used to destroy the HFC-23 has a measured DE for HFC-23 of greater than 99.998 percent, with a non-detect concentration of HFC-23 at the outlet of the device.

Implications for Destruction of Fluorinated GHGs other than HFC-23

In view of the practices described above, EPA believes that producers of fluorinated GHGs that also destroy fluorinated GHGs are already likely to verify the DEs of their destruction devices. Many facilities destroying fluorinated GHGs are likely to destroy ODS as well, meaning they must submit one-time reports providing the DE of the destruction device. Due to the HWC MACT standards, facilities that destroy ODSs that are hazardous waste test the DEs of their destruction devices, generally once every five years.

However, some fluorinated GHGs, particularly CF₄ and SF₆ are more difficult to destroy than the reference gases (e.g., monochlorobenzene) used in existing test methods for HWCs. For destruction of these compounds to occur, temperatures must be quite high,² fuel must be provided, flow rates of fuels and air (or oxygen) must be kept above certain limits, flow rates of fluorinated GHG must be kept below others, and for some particularly difficult-to-destroy chemicals such as CF₄, pure oxygen must sometimes be fed into the process. If one or more of these process requirements is not met, destruction efficiencies can drop sharply (in some cases, by an order of magnitude or more), and fluorinated GHGs will simply be exhausted from the device.

In order to verify destruction of these fluorinated GHGs, the DE would have to be verified for these compounds. Alternatively, the DE could be verified using the most-difficult-to-destroy compound actually processed by the destruction device. For example, if a destruction device were used to destroy both CF₄ and SF₆, the verification could be performed using CF₄. As noted above, verification testing performed with reference compounds such as monochlorobenzene will not verify destruction of either CF₄ or SF₆.

² For example, a temperature of 2190 degrees F is required to achieve a destruction efficiency greater than 99 percent for SF₆ (CIGRE, 2003), and the autoignition temperature for CF₄ is similarly high.

c. Equations

The total mass of fluorinated GHGs or nitrous oxide produced annually would be estimated by using equation 1 below:

$$P = \sum_{p=1}^n P_p \quad (\text{Equation 1})$$

P = mass of fluorinated GHG or nitrous oxide produced annually
 P_p = mass of fluorinated GHG or nitrous oxide produced over the period p

The total mass of fluorinated GHGs or nitrous oxide produced over the period p would be estimated by using equation 2 below:

$$P_p = O_p - U_p \quad (\text{Equation 2})$$

where:

P_p = mass of fluorinated GHG or nitrous oxide produced over the period p (metric tons)
 O_p = mass of fluorinated GHG or nitrous oxide that is measured coming out of the production process over the period p (metric tons)
 U_p = mass of used fluorinated GHG or nitrous oxide that is added to the production process upstream of the output measurement over the period p (metric tons)

Because losses may occur between the point where the total production of the fluorinated GHG is measured and the point where the fluorinated GHG is reacted as a feedstock (transformed), it may be appropriate to require that that facilities separately measure and report the production that is fed into the process for which the fluorinated GHG is used as a feedstock, using scales or flowmeters on the equipment used for that process. .

In this case, the total mass of fluorinated GHGs or nitrous oxide transformed would be estimated by using equation 3 below:

$$T = F_T - R \quad (\text{Equation 3})$$

where:

T = mass of fluorinated GHG or nitrous oxide transformed annually (metric tons)
 F_T = mass of fluorinated GHG fed into the transformation process annually (metric tons)
 R = mass of residual, unreacted fluorinated GHG or nitrous oxide that is permanently removed from the transformation process

Facilities producing fluorinated GHGs could calculate the quantities of GHG that they destroy, using equation 4 below:

$$D = F_D * DE \quad (\text{Equation 4})$$

where:

D	=	mass of fluorinated GHG destroyed annually (metric tons)
F _D	=	mass of fluorinated GHG fed into the destruction device annually (metric tons)
DE	=	Destruction Efficiency of the destruction device (fraction)

EPA is proposing that weigh scales and flowmeters be calibrated every year or sooner if an error is suspected based on mass-balance calculations or other information. Facilities could perform the verification and calibration of their scales and flowmeters during routine product line maintenance. EPA understands that some types of flowmeters that are commonly employed in chemical production, such as the Coriolis type, may require less frequent calibration.

d. Relationship of proposed requirements to current plant practices

The current best practices of the fluorinated gas industry include accurate monitoring techniques, reducing the burden of a rule.

Industry representatives from leading manufacturers were contacted on several occasions, throughout the scope of this assessment project, to ascertain current plant practices as they related to:

- general process flow streams; and
- quantitative techniques for measuring production of finished product produced, various by-product streams, waste streams, common practices, and the ability to measure process emissions.

The production process occurs in several stages. First, raw materials are transferred into a reactor. After reaction, the product goes through a distillation and purification process step, and is then held in a short term storage tank, known as a “day tank” where finished product is verified to meet a finished product specification. Once the product has met specification, it is transferred to a larger storage tank (approximately 1 MM lbs. capacity) where it is contained until, packing-off, loading and distribution.

Production yield is measured by reconciling the following streams in the process:

- measure of reactants into the reactor
- measure of waste or by-product
- measure of “finished product” collected
- amount of process losses, including fugitive emissions, lost during manufacturing, loading and transfer of finished product to customer storage tanks

Manufacturing plants use either weigh scales/load cells (a load cell is the actual “weight sensor” mechanism within a weigh scale) or flowmeters to measure the quantities of materials passing through various points in the production line. Weigh scales provide a reliable, repeatable, and accurate weight of fluorinated GHGs. Weigh scale accuracies typically are in the range of +/- 0.02 – 0.05%. This range is quoted on scale specifications by leading manufacturers and supported by bulk weighing specifications quoted as +/- 0.03-0.04%.

The most accurate type of flowmeters are Coriolis flowmeters. An advantage of Coriolis flowmeters is that it measures the mass flow rate directly, which eliminates the need to compensate for changing temperature, viscosity, and pressure conditions. Coriolis flowmeters can be purchased with accuracies quoted through specifications at +/- 0.15%, however, the more common flowmeter accuracy for industry-wide use approaches +/-0.5%.

Pro and cons to Coriolis flowmeters are as follows:

Pros:

- Higher accuracy than most flowmeters;
- Can be used in a wide range of liquid flow conditions;
- Capable of measuring hot and cold fluid flow;
- Low pressure drop; and
- Suitable for bi-directional flow

Cons:

- High initial set up cost;
- Clogging may occur and difficult to clean;
- Larger in over-all size compared to other flowmeters; and
- Limited line size availability.

Flowmeters are commonly used by some manufacturers for process control as reactants enter the reactor, and as product enters each tank. Exact flowmeter locations can be:

- in lines measuring reactants loading the reactor
- in the lines of waste / by-products
- in the line leading to the “day tank”, measuring daily finished product manufactured

Even when these flow meters are not primarily used to estimate production, they can be used for secondary production checks. Flow of pure HFC into the day tank can be collected on a daily basis. Flow meters are not placed as product is released from the reactor, as it has yet to go through the purification process. As such, the first true point in the process where measurements of a purified product without impurities can be taken is just prior to entering the “day tank”.

Whatever type of measurement device they use, fluorinated GHG producers track production at each stage of the production process. Daily and monthly mass balancing is usually completed for each product produced. Percent yield is a very important for the fluorinated GHG producers; it represents the amount of starting materials used, minus impurities sent to a destruction device, minus losses which are unaccounted for, yielding an amount of prime final product which is available for sale. This calculation is commonly done on a daily basis and then reconciled monthly with the sales of the product.

5. Procedures for Estimating Missing Data

If a facility regularly used upstream (i.e., at the entrance to the day tank) weigh scales to estimate production, a downstream estimate of production (i.e., quantity shipped) could be used in the

event that the upstream scale failed to meet an accuracy test, malfunctions, or was rendered inoperable. In this case, it might be appropriate for a facility to add some percentage (e.g., 1.5 percent) to the quantity measured using the downstream estimation procedure to compensate for losses from distribution and packaging.

In the event that neither an upstream nor a downstream methodology were feasible, a facility could calculate production based upon the consumption of reactants and assuming a complete stoichiometric conversion.

It is believed that production levels will be readily available, since business targets are reliant on accurate monitoring and reporting of production.

In cases where there is a missing value of the mass fed into the transformation processes or sent to another facility for transformation, a facility could use the arithmetic average of the quality-assured values of that parameter immediately preceding and immediately following the missing data incident.

A missing value allowance for the annual destruction device outlet concentration measurement, which is only required once a year, should not be necessary. A re-test could be performed if the data from the annual destruction device outlet concentration measurement are determined to be unacceptable or not representative of typical operations.

6. QA/QC Requirements

Typical QA/QC requirements for measuring devices include initial and periodic verification and calibration. (For example, see the requirements of EPA's Acid Rain regulations at 40 CFR Part 75.) In this case, it would be appropriate to require an initial verification of flowmeters and weigh scales and periodic calibration in accordance with the applicable industry standards. Calibration of flowmeters and scales could be performed prior to the reporting year; after the initial calibration, recalibration could be performed at least annually or more frequent if specified by the manufacturer. Under this approach, producers could perform the verification and calibration of their weigh scales during routine product line maintenance.

For the gas chromatography analytical method described under the monitoring section of this document, monthly calibration, using known certified standards should be used. The calibration involves validating accurate measurement of these fluorocarbon standards across a range of possible concentrations, depending on which process streams are being measured.

7. Reporting Procedures

The following data would be useful for confirming production calculations and/or calculating emission rates that could be compared across facilities and over time for quality control purposes:

- Total mass of fluorinated GHG or N₂O produced;
- Total mass of fluorinated GHG or N₂O transformed;
- Total mass of fluorinated GHG destroyed;
- Data on total mass of reactants fed into the production process;
- Total mass of non-GHG reactants and byproducts permanently removed from the process;

- Mass of used product added back into the production process;
- Total mass of any fluorinated GHG or nitrous oxide sent to another facility for transformation;
- Total mass of any fluorinated GHG sent to another facility for destruction; and
- The names and addresses of other facilities to which N₂O or fluorinated GHGs were sent for transformation or destruction.

For facilities destroying fluorinated GHGs, useful data would include the results of the annual fluorinated GHGs concentration measurements at the outlet of the destruction device, including: (1) the flow rate of the fluorinated GHGs being fed into the destruction device (in kg/hour); (2) the concentration (mass fraction) of fluorinated GHGs at the outlet of the destruction device; (3) the flow rate at the outlet of the destruction device (in kg/hr); and (4) the calculated emission rate based on the data provided in numbers (2) and (3). Additionally, these facilities could be required to submit a one-time report including the following: the destruction unit's DE, the methods used to record volume destroyed and to measure and record DE, and the names of other relevant federal or state regulations that may apply to destruction process. This one-time report could be very similar to that required under EPA's Stratospheric Ozone Protection regulations. The submittal of a revised report would be required if any process changes occur that affect the unit destruction efficiency or the methods used to record destruction.

8. Recordkeeping Procedures

The following records would be very useful for verifying production, transformation, and destruction estimates and related quantities and calibrations.

Owners or operators of facilities producing N₂O or fluorinated GHGs could be required to keep records of the data used to estimate production, as well as records documenting the initial and periodic calibration of the flowmeters or scales used to measure production.

Owners or operators of production facilities using N₂O or fluorinated GHGs as feedstocks could be required to keep records documenting: the initial and annual calibration of the flowmeters or scales used to measure the mass of GHG fed into the destruction device and the periodic calibration of gas chromatographs used to analyze the concentration of fluorinated GHG in the product for which the GHG is used as a feedstock.

Owners or operators of GHG production facilities that destroy fluorinated GHGs could be required to keep records documenting: the information that they send in the one-time and annual reports, the initial and annual calibration of the flowmeters or scales used to measure the mass of GHG fed into the destruction device, the method for tracking startups, shutdowns, and malfunctions and any GHG emissions during these events, and the periodic calibration of GCs used to annually analyze the concentration of fluorinated GHG in the destruction device exhaust stream, as well as the representativeness of the conditions under which the measurement took place.

9. References

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Coriolis flow meters:

Micro Motion: www.emersonprocess.com/MicroMotion/

Siemens: <https://pia.khe.siemens.com/index7625.htm>

Weigh Scales / Weigh Cells

Mettler Toledo: www.mt.com or

http://us.mt.com/mt/filters/products-applications_industrial-weighing/

American Weigh Scales: www.americanweigh.com