

45th OEWG Meeting HFC-23 Side Event

HFC-23 By-production and Emissions

Helen Tope (MCTOC Co-chair)
Nick Campbell (MCTOC Member)
on behalf of

Technology and Economic Assessment Panel (TEAP)

Outline of Presentation

- Scope of information presented
- By-product generation from chemical processes
- Chemical pathways generating HFC-23 by-product
- By-product emissions and mitigation
- Feedstock uses of HFC-23
- Emissive uses of HFC-23
- 2023 TEAP Report on decision XXXIV/7: Strengthening institutional processes with respect to information on HFC-23 by-product emissions (due September 2023)

Information is taken from TEAP Reports

- TEAP and TOCs comment on topics only through their published reports in response to requests from parties
- Includes information available from:
 - 2022 MCTOC Assessment Report
 - 2023 TEAP Progress Report, including MCTOC's Response to Decision XXXIV/5: Identification of gaps in the global coverage of atmospheric monitoring of controlled substances and options for enhancing such monitoring

By-product generation from chemical processes (1/2)

- There are several mechanisms that cause the by-production of controlled substances in production processes, including:
 - **Over or under reaction enroute to the intended product**
e.g., HFC-23 is an over fluorination of HCFC-22
 - **Presence of impurities in the feedstocks being reacted to an expected by-product**
e.g., chloroform impurity in methylene chloride/dichloromethane feedstock used to produce HFC-32 is hydrofluorinated to HFC-23
 - **Unintended side reactions where the feedstock follows a different reaction path than the one that is desired to make the product**
e.g., cleavage of carbon/carbon bond in the production of HFC-125 from perchloroethylene, with subsequent hydrofluorination of the resulting mono-carbon molecule to form HFC-23

By-product generation from chemical processes (2/2)

- By-product can be present in gaseous, liquid or solid waste streams and as impurities in products and co-products, from which there is potential for emissions.
- The design intent of most plants is to minimise by-products as they tend to have a *detrimental economic effect*, because they:
 - Consume feedstocks that cannot be (made into and) sold as final product.
 - May require additional process steps (and cost) to remove them from final product and/or to mitigate emissions of by-product e.g., thermal oxidation.
 - Make final product out of specification in some cases.

Chemical pathways generating HFC-23 by-product: HCFC-22 manufacture

- Manufacture of HCFC-22 generates HFC-23 by-production and emissions, for which Article 2J establishes destruction requirements.
 - HCFC-22 is produced for controlled uses and feedstock uses (945,508 mt, 2020).
 - HCFC-22 is largest feedstock used by considerable margin (713,536 mt, 2020).
 - About 97% of HCFC-22 feedstock is used to produce tetrafluoroethylene (TFE) and hexafluoropropylene (HFP), which are used primarily to manufacture fluoropolymers, e.g., polytetrafluoroethylene, and some HFCs and HFOs.

Chemical pathways generating HFC-23 by-product: TFE and HFP manufacture from HCFC-22 feedstock

- Manufacture of TFE and HFP from HCFC-22 feedstock generates by-production and emissions of HFC-23 and PFC-c-318 (c-C₄F₈) with very high GWP.
- These combined estimated emissions as CO₂e, without consideration of their possible abatement, are larger than estimated emissions of HFC-23 from HCFC-22 production (assuming 0.1 wt% emissions are achieved that would meet requirements to destroy to extent practicable, as per MLF supported projects).
- TFE and HFP are neither Annex C, Group I, nor Annex F substances, so HFC-23 emissions resulting from their production are not required to be destroyed under Article 2J, even if TFE/HFP production is located on same site as associated HCFC-22 feedstock production, which is more likely in newer fluorochemical facilities.

2022 MCTOC AR, Table 2.4

By-product emission or generation factors for HFC-23 and PFC-c-318 from the overall manufacturing process to produce TFE and HFP from HCFC-22*

	Emission or generation factor kg/100 kg HCFC-22	GWP (AR4)	Emissions	
			Metric tonnes	MMTCO _{2e}
Maximum allowable HFC-23 by-product emission from HCFC-22 FS (meeting requirements <i>destroyed to the extent practicable</i> in the context of Multilateral Fund-supported projects)	0.1 emission factor	14,800	710	11
HFC-23 by-product generation from TFE/HFP production based on HCFC-22 FS use	indicative generation factors MEDIUM 0.15 LOW 0.04	14,800	generation 1,040 280	generation 15 4
PFC-c-318 by-product emission from TFE/HFP production based on HCFC-22 FS use	0.3 emission factor	10,300	2,080	21

* Based on reported 2020 HCFC-22 feedstock production data, with 97% used for TFE/HFP production. HFC-23 by-product is from HCFC-22 feedstock production only, i.e., excludes non-feedstock production.

Chemical pathways generating HFC-23 by-product: Other pathways (1/2)

- Some HFCs and HFOs can be produced using process routes that may have associated emissions of HFC-23 because they use HCFC-22, TFE or HFP as feedstocks, followed by further reactions to give the final product.
 - HFCs include HFC-125 from TFE, HFC-227ea from HFP.
 - HFOs include HFO-1234yf from HCFC-22 and HFP.
- HFC-23 can also be formed as by-product during production of HFC-32 from dichloromethane.
 - There are several possible routes that lead to the formation of HFC-23 as by-product during the production of HFC-32 by fluorination of dichloromethane.

Chemical pathways generating HFC-23 by-product: Other pathways (2/2)

- HFC-23 can also be formed as by-product during production of other fluorocarbons, e.g., HFC-125, HFC-134a, HFC-143a, possibly in steps of HFO production processes.
- Preliminary data indicates generation at much lower rates than for production of HCFC-22 (2–4 % HFC-23 by weight) and HFC-32 (<0.1 % HFC-23 by weight).
- Electrochemical fluorination of alkanes can also generate fluorinated by-products, including HFC-23 (relatively minor), depending on process conditions.
- Generation rate of HFC-23 in any given process can vary as its formation depends on several factors, e.g., availability of chlorine, catalyst condition and reactor composition, temperature, pressure, presence of free radicals, etc.

By-product emissions

- Emissions are considered the release of substances into the environment, often describing gas releases of substances to the atmosphere but also substances released in solids or liquids that later transition to the atmosphere.
- For example, the HFC-23 emission from an HCFC-22 process may include both direct emissions of HFC-23 from a vent and HFC-23 degassed to atmosphere during subsequent treatment of the aqueous effluent, possibly off-site.
- The quantity of HFC-23 generated and emitted varies depending on design of the plant.
- For most, if not all, processes producing fluorinated controlled substances, HFC-23 generation is possible. For HCFC-22 production, HFC-23 generation cannot be eliminated; for other processes, very low generation rates are possible.
- For financial reasons, processes typically seek to minimise formation of unwanted by-products to maximise desired feedstock to product conversion ratios.
- In some cases, an increase in the rate of production of the desired product at the expense of a higher by-product production rate may be economically attractive.

By-product emissions mitigation

- Various techniques are available to treat unwanted by-products to minimise emission, typically end-of-pipe processes that destroy or convert the unwanted by-products to environmentally acceptable substances.
- There would usually be a need to include additional equipment (such as destruction or separation and chemical transformation technologies), with further operating and maintenance costs to the process to mitigate these unwanted by-product emissions.
- Plants with integral destruction facility to treat gaseous fluorocarbon containing vents will emit only a fraction of total generated HFC-23.
- However, lack of clear regulatory, environmental, safety or economic drivers has often meant that, once produced, these unwanted by-products are emitted unabated.

Feedstock uses of HFC-23

- A7 production for feedstock uses data reported for 2020 and 2021 is incomplete.
- HFC-23 feedstock production was reported in a quantity band between 10 to 1000 tonnes (2020).
- HFC-23 is used as a feedstock to produce halon 1301 feedstock for fipronil and other chemical production. HFC-23 emissions arise from this feedstock use.
- Recently HFC-23 is reported as a feedstock with chloroform, to convert HFC-23 to HCFC-22 and HCFC-21 (demonstration plant), in the same HCFC-22 production unit. This feedstock use will eliminate HFC-23 emissions from HCFC-22 production.

Emissive uses of HFC-23

- Production and consumption of HFC-23 for:
 - Fire suppressant
 - Low temperature refrigerant
 - Etchant and chamber cleaning in semiconductor and electronics manufacturing
- Emissive uses of chemicals with HFC-23 impurity levels leads to emissions of HFC-23, e.g., HCFC-22 uses

Decision XXXIV/7: Strengthening institutional processes with respect to information on HFC-23 by-product emissions

To request the TEAP to prepare a report for the 35th Meeting of the Parties to include:

- a) Information on the possible chemical pathways that could be used in the production of Annex C, Group I, or Annex F substances that may generate HFC-23 as a by-product;*
 - b) Compilation of information on the amount of HFC-23 generation and emissions from facilities that manufacture Annex C, Group I, or Annex F substances, the reporting of which is required under Article 7 of the Montreal Protocol;*
 - c) Best practices available to control these emissions.*
- TEAP Report in response to decision XXXIV/7 is due early September 2023 for MOP-35

Thank You

Back-up slides

Article 2J of the MP

- Article 2J of the Montreal Protocol requires that HFC-23 (Annex F, Group II) generated in facilities manufacturing Annex C, Group I or Annex F substances must be destroyed to the extent practicable using technologies approved by parties.

Most likely production emission factors

- Based on the assumptions used, the mean values for the most likely emission factors for modern day regulated manufacturing are:
 - Production 2.5% (0.9–4%)
 - Feedstock process 0.6% (0.3–0.9%)
 - Distribution by bulk supply (not pipeline) for large volume users (feedstock and equipment manufacturers) is expected to be towards the lower end of the most likely range (0.3–1.2%), as it excludes transfers to smaller packages.
 - Supply using repackaged smaller containers, and in particular disposable containers, will contribute to additional emissions depending on their relative use for each controlled substance.