Environmental risk evaluation report: 3,3,4,4,5,5,6,6,6-Nonafluorohexene (CAS no. 19430-93-4) (Perfluorobutylethylene; PFBE)

Confidential Annex

The information in this Annex comes from the EU REACH registration dossier (ECHA, 2020) unless stated otherwise (see the main evaluation report for further details).

Exposure assessment

The information in this section is based on the CSR submitted by the lead registrant to ECHA, supplemented with other information (e.g. from further dialogue with the company) where available. AGC Chemicals Europe Ltd is a member of the joint registration. This information is commercially confidential.

The volumes below are from two mass balance information supplied by AGC during this evaluation.

Year	Quantity imported (tonnes/year)
2019	84.46
2020	63.05
2021	84.78

1.1 Short description of exposure scenarios and measures for reducing emissions to the environment

1.1.1 Polymer manufacture

PFBE is imported to the UK by AGC Chemicals Europe Ltd from Japan for use as a co-monomer in the manufacture of fluorinated copolymer resins. AGC Chemicals Europe Ltd states that the realistic worse case import volume is 120 tonnes/year. The following description contains some non-confidential process information for completeness.

PTFE plant

Tetrafluoroethylene (TFE) is transferred into the reactor, then approximately 10 g per batch of PFBE is dosed from the drums it is delivered in into a storage vessel, where it is dosed directly into the reactor. The PFBE is used as a trace comonomer to control polymer properties. It is consumed during the polymerisation reaction and is incorporated into the PTFE polymer. No release is expected from the receipt, storage or transfer of PFBE at the site. The reaction is done at elevated temperature and pressure, to produce fluoropolymers. When the batch is complete, the reactor is depressurised and the remaining gaseous monomers are pumped into the gasholder. The reactor is then put under vacuum to remove more of the monomers into the gasholder. The reactor is then opened and a gas test done

to ensure that the levels of TFE are below the occupational exposure limit (the limit of detection of the gas detector is 0.05 ppm). The fluoropolymer is then removed from the reactor. Any residual PFBE is expected to be captured in the gas holder and will ultimately end up in the waste stream known as the high boiler waste which is incinerated.

The mass balance for PFBE during PTFE production supplied by AGC Chemicals Europe Ltd is shown in the table below. AGC stated that '*due to the small amounts of PFBE used in the PTFE grades, and that it is mostly consumed by polymerisation, this mass balance is based on process knowledge rather than analytical data and the values presented should be taken as indicative values'.*

	Amount (kg/year)		
	2019	**2020**	**2021**
Polymerised into the polymer (1)	59	49	80
Destroyed by incineration (2)	3	2.5	4
Emitted to atmosphere (3)	0.16	0.13	0.21

Notes

1. Assumes 95% is polymerised into polymer
2. Assumes 95% of residual PFBE remaining in the solvent at the end of the batch is purged to the gasholder, and then sent for incineration
3. Assumes 5% of residual PFBE remaining in the solvent at the end of the batch is released to atmosphere

The mass balance was derived from the quantities used and the quantity of fluoropolymer produced. There has been no recent analysis of the high boiler waste. AGC estimated that 4 kg was disposed of via incineration and 0.21 kg was released to the atmosphere in 2021.

The contents of the gasholder, which include the high boiler waste, is transferred either to the on-site incinerator or to drums for disposal at an off-site high temperature incinerator. Currently the on-site incinerator is not operational (April 2022), and so all waste is sent to Veolia. There is a specially built reception area dedicated to AGC Chemicals Europe Ltd waste at the Veolia site, where the waste is fed directly into the incinerator.

The gases the gas holder contains includes pyrolysis gases and monomer wastes from the TFE and PTFE manufacturing processes as well as other streams from other parts of the manufacturing plant. One of the constituents is perfluoroisobutene (PFIB), which is produced during the pyrolysis of HFCF-22 (R22, chlorodifluoromethane) as an un-wanted by-product from the manufacture of principle monomer, tetrafluoroethylene (TFE). PFIB is

listed as a Schedule 2 chemical weapon[1] under the Chemical Weapons Convention (CWC). The CWC is an international arms control treaty, administered by the Organisation for the Prohibition of Chemical Weapons (OPCW) based in The Hague, Netherlands. The unintentional production and presence of PFIB in the waste means that the AGC Chemicals Europe, Ltd. site undergoes regular inspections by the OPCW to ensure complete destruction of the PFIB[2]. AGC Chemicals Europe, Ltd. are also required to submit annual declarations of quantity of PFIB produced and destroyed to the UK National Authority for the Prohibition of Chemical Weapons. This level of control ensures that there are no emissions of PFBE once it is part of the high boiler waste stream.

ETFE production

PFBE is used in the manufacture of ETFE as a comonomer. A total of 40-90 L is added slowly per batch of ETFE produced.

ETFE manufacture involves two production lines and the manufacturing of ETFE consists of:

1. A polymerisation reaction which involves reaction of TFE, ethylene and PFBE in the recycled 1H-perfluorohexane in the presence of chain transfer additive (methanol) and initiator. This is carried out in the reactor at constant elevated temperature and pressure. The result is ETFE slurry. At the end of polymerisation approximately 50% of the unreacted monomer and <1% of solvent is recovered as vapour.

2. The purification process involves formation of ETFE beads in water and recovery of the remainder of the unreacted monomers as well as evaporation of approximately 99 % of the 1H-perfluorohexane and PFBE mixture, which is then condensed and recovered to solvent vessels. The recovered solvent is reused in the next batch of polymerisation. This process is carried out at elevated temperature. Recovered 1H-perfluorohexane and PFBE mixture is distilled off further at elevated temperature to reduce levels of hydrocarbon (initiator solvent). The remaining monomer is recovered at this stage.

3. Drying involves draining of water and drying ETFE beads at elevated temperature and under vacuum. Water from this process is heated to remove the alcohol and contains trace 1H-perfluorohexane and PFBE mixture. This contaminated water is then transferred to the ETFE effluent pit, an underground lined open topped tank at a temperature of 90 °C. Any gaseous 1H-perfluorohexane and PFBE mixture

[1] https://www.opcw.org/chemical-weapons-convention/annexes/annex-chemicals/schedule-2

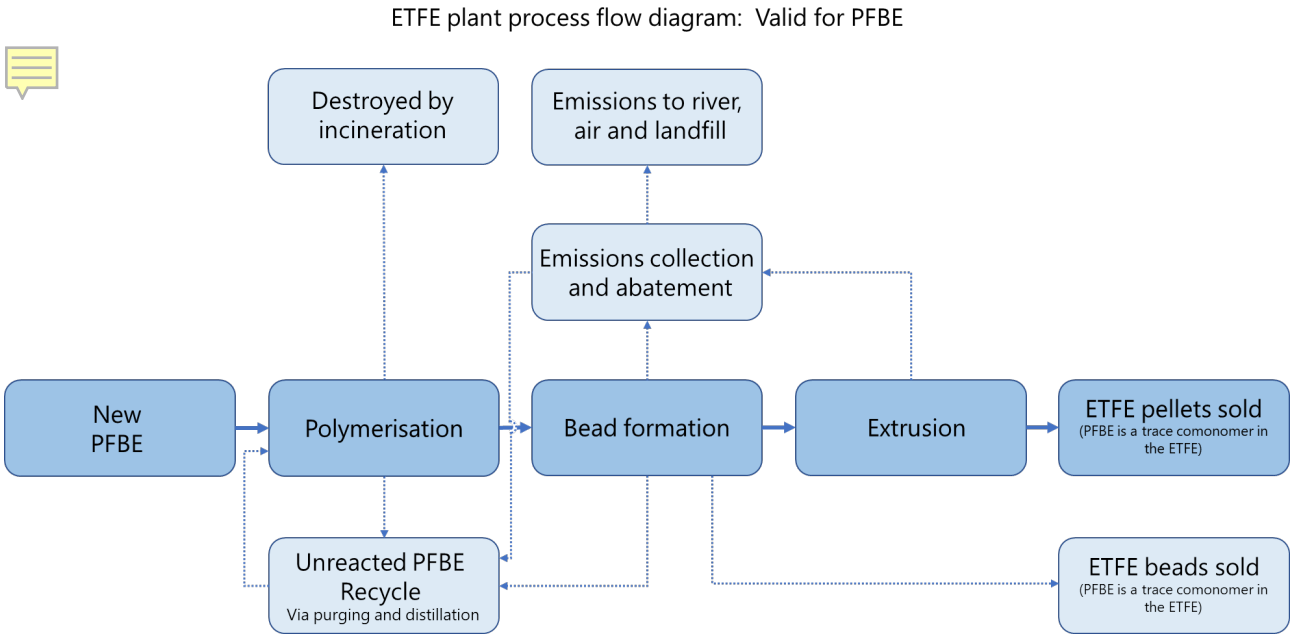
[2] https://assets.publishing.service.gov.uk/government/uploads/system/uploads/attachment_data/file/558885/OPCW_Inspection_Guidance__2016_.pdf

residing in the headspace is captured using carbon beds and recovered back to recycled solvent tanks as liquid. The water from this tank is then transferred for distillation to remove the methanol; some of the 1H-perfluorohexane and PFBE mixture is also removed in this step. The condensed water remaining after the distillation is then transferred to the ETFE waste water tank prior to transfer to the onsite effluent tank for discharge into the river Wyre.

4. Finishing process involves two types of processes. ETFE beads are either packed at this stage and sold to customers or processed further by extrusion. If processed by extrusion, ETFE is melted at high temperature in the extruder, and made into strands that are then cooled in a water bath before being cut into pellets. ETFE pellets are degassed to remove hydrogen fluoride, then packed and sold to customers.

ETFE production is a closed batch process and almost all of the 1H-perfluorohexane and PFBE mixture is recovered and reused repeatedly. The vessel is topped up with virgin 1H-perfluorohexane about once per month. The process flow diagram is shown in figure 1.

Figure 1 ETFE manufacturing process diagram



The initial mass balance calculations undertaken by AGC Chemicals Europe, Ltd. found that the quantity incorporated into the polymer was greater than the amount added.

PFBE was registered in the 100 to 1 000 tonnes/year supply band but AGC Chemicals Europe Ltd did not undertake an exposure assessment in their registration as PFBE is not classified. There is therefore no assessment of releases throughout the life cycle of the products manufactured.

The mass balance for PFBE during ETFE production supplied by AGC Chemicals Europe, Ltd. is shown in the table below:

Amount (tonnes/year)			
	2019	2020	2021
Used	84.4	63	84.7
Polymerised into the polymer (1)	89.8	70.1	89.6
Emitted to atmosphere (filling) (2)	0.45	0.36	0.45
Emitted to atmosphere (SLG) (3)	0.42	0.42	0.42

Notes

1. AGC Chemicals Europe Ltd data are being refined as currently indicating more polymerised than used. We expect close to 100 % incorporation
2. Residual amounts in drum after filling which evaporates over time.
3. Single trial and challenging analytical measurements. Have used same value for all years, and further investigations on-going. Assumes 365 days rather than 330 days operation (if based on 330 days operation, value is 0.38 t).

The mass balance was derived from the quantities used and the quantity of fluoropolymer produced. There has been no recent analysis of the high boiler waste. The estimate of a maximum of approximately 1% release of the total quantity used to atmosphere is equivalent to a release of 870 kg over a year.

The details of releases to each compartment are discussed in more detail below. The releases to the atmosphere are an estimate based on the PFBE mass balance shared by AGC Chemicals Europe Ltd.

Routes of emission to air

Most of the gaseous 1H-perfluorohexane and PFBE mixture is captured using solvent-laden-gas (SLG) recovery system on activated carbon beds and recovered back to recycled solvent tanks as liquid. Some of the substance is also released into the atmosphere from this point. Carbon bed adsorption unit is a permitted emission point. Using the data supplied in the mass balance the total release to atmosphere is 870 kg per year.

Routes of emission to water

In their updated mass balance AGC state that their expectation of '*losses to river is low, our evidence indicates the majority of PFBE is incorporated into the polymer; further investigations are on-going to confirm this'.*

As a worst case while this refinement is ongoing we have estimated releases based on the releases of 1H-perfluorohexane containing trace PFBE. The emissions to water are the process water used during the polymerisation of the ETFE. The PFBE is dissolved into the 1H-perfluorohexane, and AGC has estimated that the PFBE is present at approximately 0.5%. The release of 1H-perfluorohexane to water was estimated to be 33.443 kg/year. On the basis that PFBE is present at 0.5% the release to water of PFBE would be 167 g/year. There is significant uncertainty about the releases of both 1H-perfluorohexane and PFBE

and AGC are currently working on an analytical method for 1H-perfluorohexane to refine the release figure, which will also refine the PFBE value.

Routes of emission via landfill

In their updated mass balance AGC state that their expectation of '*losses to landfill is low our evidence indicates the majority of PFBE is incorporated in to the polymer; further investigations are on-going to confirm this. Waste ETFE is sent to landfill. Unpolymerised PFBE is not sent to landfill (except any potential residual in drums which is already counted in the emission to atmosphere)'.*

Polymer use

Based on the estimate of 0.5% of PFBE in 1H-perfluorohexane in the ETFE manufacturing plant and the release of <80 kg/year identified the 1H-perfluorohexane evaluation an estimated <400 g of PFBE is present in the ETFE on an annual basis. The worst case assumption for the release of PFBE from the polymer is that all of it is released to the atmosphere during the heat treatment during manufacture of the final products.

Summary of total releases of PFBE from PTFE and ETFE manufacture and use

Compartment	Estimated annual release kg/year
Air	**870**
Water	**0.17**