Destruction of PFAS Emissions from a Semiconductor Fabrication Facility

Introduction:

This section addresses the capture and destruction of per- and polyfluoroalkyl substances (PFAS) emissions from a semiconductor fabrication facility (semiconductor fab) across different mediums, including solid waste, wastewater, and airborne emissions. PFAS, commonly used in semiconductor manufacturing processes, can pose environmental and health risks. The section outlines methods for identifying and destroying PFAS emissions in each medium, reviews available and developing technologies in the particular context of the semiconductor industry.

PFAS capture and destruction is a dynamic field of research. There is no solution fitting all waste streams, industries and substances. It is important to ensure that the waste management methods are approved and that methods for confirming successful treatment are both available, used and kept up to date.

PFAS-Containing Waste Management

Solid Waste:

Solid waste from semiconductor manufacturing may contain PFAS residues from the use of fluorinated chemicals in lithography and etching processes. These wastes may include sludge, containers, filters, and protective equipment. In terms of back end assembly, PFAS waste is generated through PTFE use in glues and PFAS use in substrates. Solid waste can also take the form of infrastructure and equipment articles (parts and o-rings for instance) needing periodic replacement. Solid waste is transferred from the fab to a waste management company that transports it to an appropriate facility for handling and recycling when possible, or for treatment and disposal.

To destroy PFAS in solid waste, several methods are being proposed or tested, such as thermal treatment (incineration), plasma treatment, electrochemical oxidation, supercritical water oxidation and photocatalytic degradation (Berg, 2022).

Thermal treatment involves heating the waste to high temperatures to break down the carbon-fluorine bonds in PFAS. This is to date the most commonly and commercially available method. PFAS destruction in incinerators comes down to 3 parameters: temperature, turbulence (mixing) and residence time (Winchell et al. 2021). Several studies demonstrate effective destruction of PFAS above 1000°C (Pancras et al. 2016), (Kucharzyk et al. 2017), (USEPA 2020). It is critical to understand the mechanisms of destruction at stake in incinerators to identify and quantify possible additional PFAS generation during thermal treatment. Studies show that by-product PFAS generated during fluoropolymers thermal treatment in municipal kilns are not significant (Aleksandrov et al. 2019), (Gehrmann et al. 2023). There is a need to carry on research on that topic, especially when the list of substances to be monitored could be evolving.

Plasma treatment uses electrically charged gas (plasma) to generate reactive species that can degrade PFAS.

Electrochemical oxidation uses electricity to produce powerful oxidants that can oxidize PFAS.

Photocatalytic degradation uses light and a catalyst to initiate a chemical reaction that can destroy PFAS.

These methods vary in their efficiency, cost, and environmental impact, and further research is needed to optimize them for practical applications.

Identifying and destroying PFAS in solid waste involves:

- Characterization: Identifying PFAS-containing waste materials and quantifying their PFAS content
- Treatment Options: Incineration at high temperatures can thermally degrade PFAS compounds in solid waste. Pyrolysis and advanced oxidation processes (AOPs) are also potential methods
- Residue Management: Ensuring proper management of residues generated during destruction processes.

Wastewater:

Wastewater from semiconductor manufacturing may contain PFAS from the rinsing of equipment and materials that have been exposed to fluorinated chemicals. These chemicals are highly soluble and stable in water, making them difficult to remove by conventional treatment methods. To destroy PFAS in wastewater, advanced oxidation processes (AOPs) have been widely studied and applied. AOPs use strong oxidants, such as ozone, hydrogen peroxide, or hydroxyl radicals, to attack the carbon-fluorine bonds in PFAS. Those are methods that can be found in typical ultrapure water (UPW) generation plants attached to a fab, specifically in the polishing step of the system. State-of-the-art fabs water systems are set to optimize water usage with up to 50% of the used water being reclaimed and fed back into the UPW plant, hence going through those steps.

AOPs can be combined with other techniques, such as ultraviolet (UV) light, ultrasound, or catalysts, to enhance their performance. AOPs can effectively degrade PFAS in wastewater, but they may also generate harmful by-products or require high energy input.

In addition, fab wastewater treatment systems typically rely on precipitation-coagulation-clarification techniques, ultra and nanofiltration (UF), and reverse osmosis (RO). UF and RO could remove a significant fraction of long-chain PFAS and lesser amounts of short-chain PFAS into membrane concentrate streams (Boo, et al. 2018); (Jin, Peydayesh and Mezzenga 2021); (Tow, et al. 2021). Concentrates would have to be treated and disposed of (most likely by incineration).

Non-limited to the semiconductor industry, the most mature capture technology is granular activated carbon (GAC) which can remove PFAS-containing materials from wastewater. GAC is non selective and mostly effective on long chain PFAS. Anion exchange (AEX) resins can be used to complement GAC, as they are more selective and more effective for short chain PFAS. Both GAC and AEX eventually need to be replaced, producing solid waste that needs to be disposed of, by incineration. It requires specific processing and preparation steps (Berg et al. 2021). Successful incineration trials have been performed, especially monitoring PFAS by-products generation (Aston et al. 2022).

The AtWaPlas joint research project, in its pilot phase, is developing a plasma-based, low cost in situ technique. The process is in its optimization phase for large scale applications (Fraunhofer Institute for Interfacial Engineering and Biotechnology IGB, 2023). This is a very promising approach as it does not produce additional waste.

Efficiently destroying PFAS in wastewater involves:

- Characterization: Identifying PFAS compounds in wastewater discharges through analytical techniques like LC-MS/MS and GC-MS
- Treatment Options: AOPs, such as ozonation and photocatalysis, can break down PFAS compounds in wastewater. Adsorption onto activated carbon and ion exchange resins are also effective methods. In situ plasma destruction is a promising developing method.
- Regulatory Compliance: Ensuring treated wastewater complies with relevant regulatory standards before discharge.

PFAS in Airborne Emissions:

Airborne emissions from semiconductor manufacturing may contain PFAS from the evaporation or volatilization of fluorinated chemicals used in various processes. These chemicals can be emitted as gases or aerosols, and can travel long distances in the atmosphere.

Air emissions are highly scrutinized by the semiconductor industry thanks to its commitment to reduce greenhouse gas emissions (particularly PFC and HFC emissions), and also due to the hazardous nature of process gases. Point of use abatement technologies are often deployed in that regard, in combination with infrastructure-wide exhaust systems (Semiconductor PFAS Consortium Plasma Etch and Deposition Working Group 2023).

To destroy PFAS in airborne emissions, several abatement methods have been suggested or tested, such as adsorption, catalytic combustion, catalytic hydrolysis, electric discharge, non-thermal plasma destruction and chemical upgrading (Chang and Lee 2004, Shih et al. 2002). Adsorption uses porous materials, such as activated carbon or zeolites, to capture PFAS from the air stream. Catalytic combustion uses a catalyst such as PT/ZrO_2 – SO_4, Ni pyrophosphate or a $AlPO_4$-AL2O_3 system to facilitate the oxidation or hydrolysis of PFAS gases at lower temperatures than thermal combustion (Feaver and Rossin 1999, Onoda et al. 2005 and Jeon et al. 2003). Non-thermal plasma uses electrically charged gas (plasma) to generate reactive species that can degrade PFAS. These methods have different advantages and disadvantages, such as selectivity, capacity, regeneration, and energy consumption (Beu, Raoux, et al. 2019).

The combination of different approaches can add the advantages of the destruction technologies, reducing the emissions further (Sheldon and Crimmin 2022).

Abatement manufacturers continue to develop new and improved abatement technologies and, as such, it is possible to demonstrate efficacy in specific semiconductor applications with experimental data. Each POU abatement technology has additional utility use, space, cost, operation, safety, air and wastewater considerations that require application-specific evaluations (Beu 2005).

Managing PFAS in airborne emissions involves:

- Characterization: Identifying sources of PFAS emissions in semiconductor fab processes
- Treatment Options: Using air pollution control equipment, such as scrubbers or thermal oxidizers, to capture and destroy PFAS compounds in exhaust gases
- Monitoring and Compliance: Regularly monitoring airborne emissions and ensuring compliance with air quality regulations.

Conclusion

Destruction of PFAS emissions from semiconductor fabs is crucial to prevent environmental and health impacts. PFAS can potentially be emitted in solid waste, wastewater and air emissions. Waste management strategies and infrastructures are already in place in the fab ecosystem, however they are not especially designed to efficiently capture and destruct PFAS. Identification and monitoring technologies will need to be developed and implemented in case of regulation.

A few capture technologies are available and compatible with industrial applications, namely granular activated carbon (GAC) and anion exchange membrane (AEX). They have to be optimized for PFAS. Developing technologies are also identified, but are years away from industrialization. Some are very promising, especially if combined or used in synergy with others. Often, capture technologies will produce concentrates needing proper treatment and destruction; this is particularly the case for GAC and AEX.

The mainstream destruction technology is incineration. Research efforts are needed to verify that destruction occurs without potentially harmful by-products being generated. Recent studies have shown promising results in that sense, in real conditions using municipal-type kilns. Other destruction technologies require optimization, validation, or research.

Given support and progress in PFAS capture and destruct technologies, the semiconductor manufacturing industry could leverage existing waste management strategies, combined with its expertise of challenging and advanced processes. Implementing appropriate technologies and adhering to regulatory standards will contribute to sustainable management of PFAS emissions. There is a need for supporting research and development in that field and an opportunity to leverage the semiconductor industry waste management strategies and infrastructures, combined with expertise of challenging process management for successful implementation.

References:

Aleksandrov et al. 2019 - Waste incineration of Polytetrafluoroethylene (PTFE) to evaluate potential formation of per- and Poly-Fluorinated Alkyl Substances (PFAS) in flue gas

Aston et al. 2022 - Removal of PFAS from Wastewater through Adsorption and Sorbent Incineration

Berg et al. 2022 - Developing innovative treatment technologies for PFAS-containing wastes

Beu 2005 - Reduction of Perfluorocompound (PFC) Emissions: 2005 State-of- the-Technology Report

Beu, Raoux, et al. 2019 - "Chapter 6 Electronics Industry Emissions." In 2019 Refinement to the 2006 IPCC Guidelines for National Greenhouse Gas Inventories Volume 3: Industrial Processes and Product Use

M. B. Chang and H. M. Lee, Catal. Today, 2004, 89, 109–115 - Abatement of perfluorocarbons with combined plasma catalysis in atmospheric-pressure environment

W. B. Feaver and J. A. Rossin, Catal. Today, 1999, 54, 13–22 – The catalytic decomposition of CHF3 over ZrO2-SO4

Gehrmann et al. 2023 - Pilot-Scale Fluoropolymer Incineration Study: Thermal Treatment of a Mixture of Fluoropolymers under Representative European Municipal Waste Combustor Conditions

J. Y. Jeon, X.-F. Xu, M. H. Choi, H. Y. Kim and Y.-K. Park, Chem. Commun., 2003, 1244–1245 – Hydrolytic decomposition pf PFCs over $AlPO_4$-Al_2O_3 catalyst.

Kucharzyk et al. 2017 - Novel treatment technologies for PFAS compounds: A critical review

Pancras et al. 2016 - Environmental fate and effects of poly and perfluoroalkyl substances (PFAS)

H. Onoda, T. Ohta, J. Tamaki and K. Kojima, Appl. Catal., A, 2005, 288, 98–103 – Decomposition of triflouromethane over nickel pyrophosphate catalysts containing metal cation

Sheldon, Crimmin, Chem. Soc. Rev, 2022, 51, 4977-95 - Repurposing of F-gases: challenges and opportunities in fluorine chemistry.

M. Shih, W.-J. Lee, C.-H. Tsai, P.-J. Tsai and C.-Y. Chen, J. Air Waste Manage. Assoc., 2002, 52, 1274–1280 - Decomposition of SF6 in an RF Plasma Environment,

Semiconductor PFAS Consortium Plasma Etch and Deposition Working Group 2023 - PFAS-Containing Fluorochemicals Used in Semiconductor Manufacturing Plasma-Enabled Etch and Deposition

USEPA 2020 -Per- and Polyfluoroalkyl Substances (PFAS): Incineration to manage PFAS waste streams background

Winchell et al. 2021 - Per- and polyfluoroalkyl substances thermal destruction at water resource recovery facilities: A state of the science review