June 2, 2023

Comments for Annex XV Restriction Report on the Manufacture, Placing on the Market and Use of PFASs; Evidence for Question 3: Emission in the End-of-Life Phase.

Submitted via the webform made available by the European Chemicals Agency at https://comments.echa.europa.eu/comments_cms/AnnexXVRestrictionDossier.aspx?RObjectId=0b0236e1885e69de

This information is submitted on behalf of the American Chemistry Council's (ACC) Performance Fluoropolymer Partnership (hereafter "PFP"), whose members include some of the world's leading manufacturers, processors, and users of fluoropolymers, including fluoroplastics, fluoroelastomers and perfluoropolyether polymers.[1] The PFP's mission is to promote the responsible production, use, and management of fluoropolymers. We invest in research to support our mission and inform a scientifically sound, risk-based approach to regulation.

This submission describes an ongoing project to characterize the fate of fluoropolymers when products containing them are combusted in municipal solid waste (MSW) waste-to-energy incineration plants in Europe and the United States. The results of this study will be critical for ECHA's assessment of the need to regulate fluoropolymers end-of-life in MSW streams and will inform our shared goals of protecting human health and the environment.

The study methodology and results to be published in peer reviewed journals in 2024 will characterize the fate of fluoropolymers in municipal waste combustion facilities across a wide range of operating conditions typical of those used throughout Europe and the United States.

Study Overview

The study will evaluate the destruction of carbon-fluorine bonds in Polytetrafluoroethylene (PTFE; CAS # 9002-84-0), Polychlorotrifluoroethylene (PCTFE; CAS # 9002-83-9), Fluorinated ethylene propylene (FEP; CAS # 25067-11-2), Polyvinylidene fluoride (PVDF; CAS 24937-79-9), and Fluoroelastomer (FFKM; CAS # 64706-30-5) separately combusted under operating conditions representative of full-scale MSW waste-to-energy incineration plants in the European Union. We will conduct fluoropolymer combustion tests at three different temperatures to demonstrate the degree to which carbon-fluorine bonds and carbon-chlorine bonds in the study polymers are converted to HF and HCl in the process. Such conversion will be demonstrated by rigorous fluorine and chlorine analysis and mass balances for each test condition.

[1] https://fluoropolymerpartnership.com/

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Assessment of Existing Literature

A review of existing literature and peer reviewed studies informed the selection of test conditions characteristic of normal MSW waste-to-energy incineration plant operating conditions. The first phase of the study was a literature review which evaluated existing publications for assessment of MSW incinerator operating conditions. A summary of these conditions (based on key publications Giraud *et al.* (2021)[2] and Neuwahl *et al.* (2019)[3]) are:

- Reactor Temperature: 850 – 1150 C
- Oxygen in the Exhaust: 6-13 % (dry basis)
- Gas Residence Time: 2 sec
- Moisture: >10%

Appendix 1 contains a list of relevant literature reviewed during the course of the study's initial phase. We expect this project to contribute significantly to our collective understanding of the fate of fluoropolymers under operating conditions representative of real-world MSW waste-to-energy incineration plants.

Study Analytics

A suite of analytical tests is planned to fully characterize the fate of carbon-fluorine bonds and carbon-chlorine bonds in the study polymers converted to HF and HCl. Such conversion will be demonstrated by rigorous analytical analyses and fluorine and chlorine mass balances. The study will include extensive quality assurance and quality control measures, including collection and analysis of blanks to check for external PFAS contamination, instrument calibrations, and oversight by a third-party quality assurance firm.

The study will assess transport efficiency across the reactor system. We will validate that cross-contamination or impurities from outside the test polymers do not compromise results. Measurements will be taken at prescribed temperatures to evaluate HF formed during combustion of a suitable fluorinated high purity standard as the fluorine source. By doing so we can assess fluorine transport efficiency across reactor system via mass balance and determine the need for post-experiment steam cleaning to return to baseline conditions. Similarly, the study will assess HCl formation during combustion of a suitable chlorinated high purity standard to assess chlorine transport efficiency across reactor system via mass balance.

The study will utilize comprehensive sampling and analysis to evaluate the effect of operating conditions (e.g., temperature) on generation of products of incomplete combustion

[2] Giraud, R., Taylor, P. Huang, P., 2021. *Combustion operating conditions for municipal Waste-to-Energy facilities in the U.S..* Waste Management (132) 124-132. https://doi.org/10.1016/j.wasman.2021.07.015.
[3] Neuwahl, F., Cusano, G., Gomex Benvanides, J., Holbrook, S., Roudier, S., 2019. *Best Available Techniques (BAT) Reference Document for Waste Incineration: Industrial Emissions Directive 2010/75/EU (Integrated Pollution Prevention and Control)*, EUR 29971 EN. European IPPC Bureau, Joint Research Centre, Luxembourg.

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(PICs). Fourier transform infrared spectroscopy (FTIR) and GC/MS (gas chromatography/mass spectrometry) will quantify generation of major halogenated reaction products. Aqueous impinger solution will be analyzed for C4 – C18 perfluorocarboxylic acids (PFCAs), C4 – C14 perfluorinated sulfonic acids (PFSAs), trifluoroacetic acid, and other nonpolymer PFAS via liquid chromatography with tandem mass spectrometry. Halides in impinger solution will be determined via ion chromatography (and/or ion-specific electrode). Continuous gas analysis will provide real-time measurement of combustion products including O_2, CO, and CO_2.

The PFP will supply ECHA with the results of this study as they become available as early as this coming September. The breadth of analytical results will provide definitive analysis of the fate of fluoropolymers in municipal waste-to-energy plants and mitigate the need for further consideration of regulatory action for the end-of-life of fluoropolymer chemistries. We will also provide information on the employed analytical methods in our future submissions.

We intend to demonstrate confirmation via full-scale MSW waste-to-energy incinerator testing to begin as early as Q4 2024.

Sincerely,

Jay West
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Appendix 1

Bench-scale Studies

Baker, Jr., B.B. and Kasprzak, D.J. "Thermal Degradation of Commercial Fluoropolymers in Air," Polymer Degradation and Stability 42, 1993, pp. 181-188.

Bhadbury, P.S., Sigh, S., Sharma, M., and Palit, M., "Flash Pyrolysis of Polytetrafluoroethylene in a Quartz Assembly," Journal of Analytical and Applied Pyrolysis, 78, 2007, pp. 288-290.

Conesa, J.A. and Font, R. "Polytetrafluoroethylene Decomposition in Air and Nitrogen, " Polymer Science and Engineering and Science, 41, 2001, pp. 2137-2147.

Ellis, D.A., Mabury, S.A., Martin, J.W., and Muir, D.C.G. "Thermolysis of Fluoropolymers as a Potential Source of Halogenated Organic Acids in the Environment," Nature 412, 2001, pp. 321-324.

Ellis, D.A., Martin, J.W., Muir, D.C.G., and Mabury, S.A. "The Use of 19F NMR and Mass Spectrometry for the Elucidation of Novel Fluorinated Acids Evolved in the Thermolysis of Fluoropolymers," Analyst 128, 2003, pp. 756-764.

Garcia, A.N., Viciano, N., and Font, R. "Products Obtained in the Fuel-rich Combustion of PTFE at High Temperature," Chemosphere 80, 2007, pp. 85-91.

Gustavsson, J. P. R., Segal, C., Dolbier, W.R., Ameduri, B., and Kostov, G. "Combustion and Thermal Decomposition of Fluorinated Polymers," Combustion Science and Technology, 178, 2006, 2097-2114.

Morisaki, S. "Simultaneous Thermogravimetry-Mass Spectrometry and Pyrolysis-Gas Chromotography of Fluorocarbon Polymers," Thermochimica Acta, 25, 1978, pp. 171-183.

Ochi, K., Kawano, M., Matsuda, M., and Morita, M. "Thermal Degradation Products of Polytetrafluoroethylene (PTFE) under Atmospheric Condition," Organohalogen Compounds, 70, 2008, pp. 002090-002093.

Paciorek, K. L., Kratzer, R.H., and Kaufman, J. "Oxidative Thermal Degradation of Polytetrafluoroethene," Journal of Polymer Science, 11, 1973, pp. 1465-1473.

Taylor, P.H., Yamada, T., Striebich, R.C., and Graham, J.L. "Incineration Testing Program: Laboratory scale incineration testing of fluoropolymers," University of Dayton Research Institute Final Report, U.S. EPA Docket No. OPPT-2003-0071, October 2009.

Taylor, P.H., Yamada, T., Striebich, R.C., and Graham, J.L., and Giraud, R.J. "Investigation of Waste Incineration of Fluorotelomer-Based Polymers as a Potential Source of PFOA in the Environment," Chemosphere 110, 2014, pp. 17-22.

Yamada, T., Taylor, P.H., Buck, R.C., Kaiser, M.A., and Giraud, R.J. "Thermal Degradation of Fluorotelomer Treated Articles and Related Materials," Chemosphere 61, 2005, pp. 974-984.

Vjacheslav, V., Zuev, V.V., Bertini, F., and Audisio, G. "Investigation on the Thermal Degradation of Acrylic Polymers with Fluorinated Side Chains," Polymer Degradation and Stability, 91, 2006, pp. 512-516.

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Pilot-scale Studies

Aleksandrov, K., Gehrmann, H., Hauser, M., Matzing, H., Pigeon, D., Stapf, D., Wexler, M. "Waste Incineration of Polytetrafluoroethylene (PTFE) to Evaluate Potential Formation of Per- and Poly- Fluornated Alkyl Substances (PFAS in Flue Gas", Chemosphere 226, 2019, pp. 898-906.

Lemieux, P., Strynar, M., Tabor, D., Wood, J., Cooke, M., and Rayfield, B. "Emissions of Fluorinated Compounds from the Combustion of Carpeting," International Conference on Incineration and Thermal Treatment Technologies, Phoenix, AZ, May 2007.

Full-scale Studies

Barr Engineering, "Results of the April 26-27, 30 and May 1-2, 2018 PFAS Emissions and RTAP Tests Performed on the MA, MS and QX Towers at Saint Gobain Performance Plastics, " Revised May 2019.

Beahm, C., "2018 Results for Per- and Polyfluoroalkyl Substances (PFAS) Analyses Performed by U.S. EPA Office of Research & Development for Samples Collected in Southern New Hampshire, April 2019.

Beahm, C., "PFAS Emissions Investigation Saint-Gobain Performance Plastics, Merrimack, NH", presentation to NACAA Fall Membership Meeting, Cleveland, OH, October 16, 2018.

Clarke, F.B., Van Kuijk, H., Valentine, R., Makovec, G.T., Seidel, W.C., Baker, Jr., B.B., Kasprzak, D.J., Bonesteel, J.K., Janssens, M., and Herpol, C. "The Toxicity of Smoke from Fires involving Perfluoropolymers: Full- scale Fire Studies" Journal of Fire Sciences, 10, 1992, pp. 488-527.

Delucia, M.A., and Wolfe, H.E. "Refractories to Contain Fluorinated Waste Streams", Proceedings of the 1999 International Conference on Incineration and Thermal Treatment Technologies, 1999.

Gentile, T., "Per & Polyfluoroalkyl Substances (PFAS) Emissions Test Results - McCaffrey Street PFAS Emissions Characterization Study," presentation to Hoosick Area Community Participation Work Group, December 18, 2019.

Gentile, T. "Results of PFTE Sintering Oven Emissions Characterization Study", Memorandum to Steven Flint, Director, Division of Air Resources, December 17, 2019.

Ryan, J., Krebs, K., Riedel, t., Offenberg, J., Nessley, L., Wright, B., and Phelps, L. "Joint ORD/NYSDEC Saint Gobain PTFE Sintering Facility Emissions Characterization Study", December 2019 (Hoosick Falls, NY).

Literature Reviews

J. Bakker, B. Bokkers, and M. Broekman, "Per- and polyfluorinated substances in waste incinerator flue gases, RIVM report 2021-0143," National Institute for Public Health and the Environment (RIVM), Bilthoven, Netherlands, 2021.

Huber, S., Schmidbauer, N., Moe, M.K., Hansen, G.H., and Herzke, D. "Emissions from Incineration of Fluoropolymer Materials - A Literature Survey", Norwegian Institute for Air Research, 2009.

Puts, G., Crouse, P., and Ameduri, B. "Thermal Degradation and Pyrolysis of Polytetrafluoroethylene," Handbook of Fluoropolymer Science and Technology, John Wiley & Sons, 2014, pp. 81-104.

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