Regarding:
ANNEX XV RESTRICTION REPORT – Per- and polyfluoroalkyl substances (PFASs)

Comments and Information about Mineralization of PFASs
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In the second paragraph under the subtitle “Concern” in the section “Summary” in Page 1 of ANNEX XV RESTRICTION REPORT – Per- and polyfluoroalkyl substances (PFASs), it says that “When these substances and their degradation products continue to be released to the environment, the concentration in the environment will increase as mineralization under natural conditions does not take place for the PFASs in the scope of this restriction proposal.” .

So, whether the substances can be mineralized is one key issue in the restriction proposal, a base for proposing the restriction proposal, and an important and key factor for considering whether the restriction proposal will enter the next phage or not. It says that these substances can not be mineralized. But, in fact, as I know, these substances can be mineralized according to recently-published articles (Jin Hamaura et al’s research article published in January 2023, and Brittany Trang et al’s research article published in August 2022).

The following are the two scientific articles:

1. Jin Hamaura, Ryo Honma, Hisao Hori, Abdelatif Manseri, Bruno Ameduri, Efficient fluoride recovery from poly(vinylidene fluoride), poly(vinylidene-fluoride-co-hexafluoropropylene) copolymer and poly(ethylene-co-tetrafluoroethylene) copolymer using superheated water with alkaline reagent, European Polymer Journal, Volume 182, 3 January 2023, 111724.
https://doi.org/10.1016/j.eurpolymj.2022.111724 (hereinafter, “Article 1”)
2. Low-temperature mineralization of perfluorocarboxylic acids | Science, BRITTANY TRANG, et al, SCIENCE, 18 Aug 2022, Vol 377, Issue 6608, pp. 839-845
DOI: 10.1126/science.abm8868 (hereinafter, “Article 2”)

Article 1 discloses a new technique for mineralization of the fluoropolymers, i.e., PVDF, poly(VDF-co-HFP) and ETFE. These polymers can decomposed to F^-, further formed artificial fluorspar. This is a transformation from organic fluorine to inorganic fluorine. So, based on this new mineralization technique, fluoropolymers can re-used in a recycling way. Fluoropolymers can be produced, used and recycled in a close loop and bring benefits to human beings without harm to the environment and human health.

The following is the experimental data obtained from the superheated water treatment of PVDF and copolymers in Article 1. This is a copy of Table 1 of Article 1.

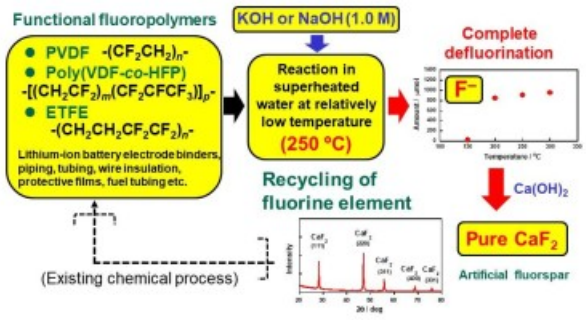
Table 1
Products from superheated water treatment of PVDF and copolymers.[a]

Entry	Polymer[b]	Alkaline reagent [Conc.(M)]	Coexisting gas	*T* (°C)	*P* (MPa)	F^- (μmol) [yield (%)]	TOC (μmol) [ratio (%)]	CO_2 (μmol) [yield (%)]
1	PVDF	none	Ar	250	4.4	1.4 [0]	3.7 [0]	2.1 [0]
2	PVDF	KOH [1.0]	Ar	250	4.4	910 ± 4 [c] [95 ± 1]	144 ± 25[c] [15 ± 3]	0.5 ± 0.0 [c] [0]
3	PVDF	NaOH [1.0]	Ar	250	4.4	858 [89]	225 [24]	0.4 [0]
4	PVDF	KOH [1.0]	Ar	200	2.3	846 [88]	32 [3]	0.2 [0]
5	PVDF	KOH [1.0]	O_2	250	4.1	866 [90]	149 [16]	0.4 [0]
6	Poly(VDF-*co*-HFP)	KOH [1.0]	Ar	250	4.4	934 [100]	188 [21]	0.2 [0]
7	Poly(VDF-*co*-HFP)	KOH [1.0]	O_2	250	4.2	951 [101]	200 [22]	0.3 [0]
8	ETFE	KOH [1.0]	Ar	250	5.2	903 [98]	243 [26]	0.1 [0]
9	ETFE	KOH [1.0]	Ar	200	2.3	1.1 [0]	29 [3]	0.1 [0]

[a] Internal volume of the autoclave, 31 mL; initial solution volume, 10 mL; reaction time, 6 h.
[b] Charged weight, 30 mg.
[c] Obtained from two replicate experiments under the same reaction conditions.

As seen in the table, F^- ion was formed in the treatment of these polymers using superheated water with alkaline reagent. In Entry 2, the F^- amount was 910 umol, corresponding to 95% yield, relative to the amount of fluorine atoms 959 umol in the initial PVDF, which is an almost complete mineralization, when KOH was employed. In Entry 3, NaOH induced the defluorination of PVDF to form F^-, when NaOH was employed likely. In Entry 4, Elevating temperature to 200℃dramatically enhanced the F^- amount, reaching 846 umol, which corresponds to 88% yield. In Entry 5, under the combination of OH^- and O_2, the F^- amount was 866 umol, which corresponds to 90% yield. In Entries 6 and 7, the decomposition of poly(VDF-*co*-HFP) was shown. In Entry 6, the fluorine content in initial poly(VDF-*co*-HFP) polymer was completely mineralized (100% yield) with 1.0M of KOH, at 250℃, under Ar for 6h. In Entry 7, the data was obtained under the combination of OH^- and O_2. In Entry 8, the fluorine content in initial ETFE was completely mineralized, in which the F- amount was 903 umol, corresponding to 98% yield.

In Appendix A. Supplementary material of this article, it provided the following graph to explain the recycling of fluorine element based on the new process. The process makes the fluorine element of fluoropolymers recycle by using 1.0 M of KOH or NaOH in superheated water at a relatively low temperature (250℃） to treat fluoropolymers, forming fluorine ions, and further transforming artificial fluorspar.



Therefore, based on this new technique, the fluorine element of fluropolymers can used in a recycling way in a closed loop without environmental harm. Therefore, there is no harm to human beings.

Article 2 is a research article published in Science, which disclosed the mineralization of ten of perfluorocarboxylic acids (PFCAs) and perfluoroalkyl ether carboxylic acids (PFECAs) through a sodium hydroxide-mediated defluorination pathway. PFCAs decarboxylation in polar aprotic solvents produced reactive perfluoroalkyl ion intermediates that degraded to fluoride ions within 24 hours.

Fig. 1 of Article 2 shows the degradation pathways:

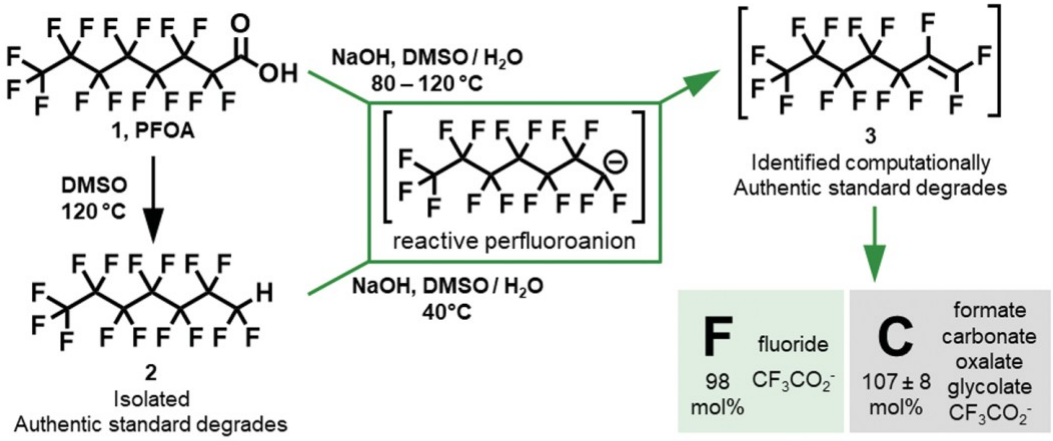


Fig. 1. Overview of degradation pathways identified in this study. Heating PFCAs in polar aprotic solvents such as DMSO decarboxylates them to 1H-perfluoroalkanes. When this reaction was performed in the presence of NaOH, the PFCA mineralized to fluoride, sodium trifluoroacetate, and nonfluorinated carbon-containing products. The 1H-perfluoroalkane underwent the same degradation process at even lower temperatures. Computational studies identified the corresponding perfluoroalkenes as likely intermediates, and an authentic standard of the seven-carbon perfluoroalkene was competent for the degradation.

In this figure, PFOA was decarboxylated and defluorined in a mixture of DMSO and water, in the presence of NaOH, at mild temperature (80 to 120 ℃), and ambient pressure.

As to Article 2, the last page has the following comments:

Forever chemicals' Achilles' heel
Per- and polyfluoroalkyl substances (PFAS) have been referred to as "forever chemicals" because of their resistance to most biological and chemical degradation mechanisms. Most current methods use very harsh conditions to decompose these compounds. Trang *et al*. found that there is a potential weak spot in carboxylic acid–containing PFAS: Decarboxylation in polar, non-protic solvents yields a carbanion that rapidly decomposes (see the Perspective by Joudan and Lundgren). The authors used computational work and experiments to show that this process involves fluoride elimination, hydroxide addition, and carbon–carbon bond scission. The initial decarboxylation step is rate limiting, and subsequent defluorination and chain shortening steps occur through a series of low barrier steps. The procedure can accommodate perfluoroether carboxylic acids, although sulfonic acids are not currently compatible. — MAF

This indicates that Article 2 found the weakness of PFAS to eliminate the fluoride ions.

After the publication of Article 2, there were some comment articles published:

1. Shira Joudan and Rylan J Lundgren, Taking the "F" out of forever chemicals, SCIENCE, 18 Aug 2022, Vol 377, Issue 6608, pp. 816-817
DOI: 10.1126/science.add1813
2. Will Sullivan, Scientists Find a New Technique for Breaking Down 'Forever Chemical', August 23, 2022, Smart News
SCIENCE□18 Aug 2022 Vol 377, Issue 6608,pp. 816-817
DOI: 10.1126/science.add1813
3. "Forever chemicals" destroyed by simple new method (2022, August 18), https://phys.org/news/2022-08-chemicals-simple-method.html.

Therefore, based on my recently-obtained knowledge in this field, I think per- and polyfluoroalkyl substances (PFAS) can be mineralized, whether it is a small molecule or a large molecule. All the PFASs as organic fluorine substances may form fluorine ions, and transform into inorganic fluorine. Therefore, the use of fluorine element can be realized in a closed loop in the future. Namely, inorganic fluorine can be transformed into organic fluorine, and organic fluorine can be transformed into inorganic fluorine, and inorganic fluorine can re-used and transformed into organic fluorine again. This way means a closed loop, and does not have harm to the environment and human health.