

Trials of Burning PFASs Containing Wastes in a Waste Incinerator and Cement Kiln Assessed against Stockholm Convention Objectives

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1 Introduction

Products or materials containing high levels of persistent organic pollutants (POPs) become POPs wastes when they become obsolete and/or cannot be used anymore due to their ban restrictions under the Stockholm Convention. POPs waste has to be “Disposed of in such a way that the persistent organic pollutant content is destroyed or irreversibly transformed so that they do not exhibit the characteristics of persistent organic pollutants”^{1,2}. They must be destroyed in environmentally sound manner by technologies listed in the General Technical Guidelines for POPs wastes which have been adopted by the Basel Convention Conference of Parties¹. This applies to all wastes containing POPs listed in Annexes A, B or C of the Stockholm Convention. However, some POPs can be harder to destroy or irreversibly transform, and for assessing the performance of the ESM operations, a minimum destruction efficiency (DE) of 99.999 per cent, with a minimum destruction and removal efficiency (DRE) of 99.9999 per cent as a supplementary requirement, provides practical benchmark parameters for assessing the effectiveness of POPs destruction technologies according to the above mentioned Basel Guidelines¹.

“DE is the percentage of POP content within the waste destroyed or irreversibly transformed by a particular technology, calculated on the basis of the mass of the POP content within the waste, minus the mass of the remaining POP content in the gaseous, liquid and solid residues, divided by the mass of the POP content within the waste, i.e., $DE = (POP \text{ content within waste} - POP \text{ content within gas, liquid and solid residual}) / POP \text{ content within the waste}$. Destruction removal efficiency (DRE) only considers emissions to air and is the percentage of original POPs irreversibly transformed and removed from gaseous emissions”¹.

The group of per- and polyfluoroalkyl substances (PFASs) including PFOS, PFOA and PFH_xS, which are already listed under the Stockholm Convention, are chemicals which are hard to destroy as they are designed to withstand high temperatures without degradation. It is also very difficult to evaluate their destruction because they may be transformed to other PFASs which are not listed under the Stockholm Convention but may represent a comparable threat to human health and environment. Recent US EPA Interim Guidance on Destruction of PFASs suggested, emission studies of PFASs waste destruction trials, particularly for potential products of incomplete combustion (PICs), “are largely incomplete due to lack of validated sampling and measurement methods for the potentially large number of fluorinated and mixed halogenated organic compounds that might be formed”³.

This brief study is focused on evaluation of publicly available data about trials of burning wastes containing PFASs, in particular those listed under Stockholm Convention. These trials were undertaken in two high temperature operations based in Australia – a cement kiln and a high temperature hazardous waste incinerator.

2 Materials and Methods

This analytical examination of PFAS waste trials burns (with an objective of complete destruction) in two combustion operations in Australia is based on publicly available data for the two separate trials.

Trials of solid and liquid wastes containing PFASs, PFOS and PFOA in particular, were conducted in February 2019 in a high temperature hazardous waste incinerator in South Australia. Trials with liquid waste were described in the report as follows: “First day 410L of PFAS contaminated surface water was injected during 6.53h of operation, an average flow rate of 62.76 L/h. The waters were co-incinerated with 3,829kg of medical waste and 113kg of confidential waste. ... Due to the low flow rate and the number of operational issues encountered, this trial day was not considered as representative but corrective actions were identified and implemented for the following trial day.”

On the following day, “...1,990L of PFAS contaminated surface water was injected during 9.67h of operation, an average flow rate of 205.86 L/h. The waters were co-incinerated with 5,533kg of medical waste”⁴.

The trial report description for the solid waste trial burn of spent activated carbon contaminated with PFASs was reported as follows: “2,618kg of contaminated carbon was incinerated together with 2,975kg of medical waste during 9h40 min of operation”⁵. The solid waste trial required a minimum primary combustion chamber (step 1) and post combustion chamber (step 2) temperature of 850° C. There were problems maintaining this temperature in the preliminary combustion chamber (step 1) due to cooling caused during the addition of medical waste loads and the full ‘ash push’ from step 1 to step 2. After identifying these factors at the 14th load cycle of 55 cycles and rectifying the anomalies by spacing PFAS loading intervals further apart, temperature compliance at step 1 was achieved and post combustion chamber temperatures of around 1100° C were maintained for most of the trial.

Cement Australia's, Fisherman's Landing Cement Kiln in Gladstone Queensland completed a trial for the destruction of aqueous firefighting foam (AFFF) concentrate containing PFASs in December 2017. The trial represented the first stage of the AFFF co-processing trial, whereby low level fluoride is introduced to the clinker manufacturing kiln through the main burner⁶. Many AFFF formulations currently contain complex combinations of PFASs⁷. The cement kiln consists of a rotary kiln inclined 3-4° from horizontal rotated 1-4 times per minute. During standard operation, a coal fired preheater heats the raw meal before it is fed to the main kiln where typically a combination of solvent based alternative fuel, industrial wastewater (IWW), coal and calcined ash is burned to provide the heat to calcine the raw meal. During the trial burn IWW and calcined spent cell liner were being used as alternative fuels in the kiln. Operating conditions of the main burner of the rotary kiln were claimed as temperatures >1450°C for material and >1800°C for flame temperature. The residence time was claimed to be >12-15 seconds at >1200°C and >5-6 seconds at >1800°C. Cement Australia states that 9.62 tonnes of 0.3% F concentration firefighting foam was co-processed during the trial. The fire-fighting foam was added at a rate of up to 1.08 tph into the main burner⁶.

Nineteen and twenty-seven PFAS species were measured during trials in the Australian hazardous waste incinerator and cement kiln respectively.

We attempted to evaluate published trial data against the POP waste destruction requirements of both the Basel and Stockholm Conventions as they are specified in General Technical Guidelines for POPs Waste¹, with a focus on DE and DRE in particular. We also compared results of the Australian trials with information and data in literature related to PFASs destruction and/or their generation by waste incineration and/or co-processing in cement kilns.

3 Results

Hazardous waste incinerator trials: These trials consisted of separate trial burns of two different PFAS waste types, solid and liquid. No PFAS was found in the fly ash during either trial in the high temperature hazardous waste incinerator as described in the trial reports^{4,5}. During a representative trial burning *liquid* PFASs waste PFBA, PFOA and PFPeA were detected in the stack, PFPeA was also detected in the blank stack samples. Some PFAS was detected in the bottom ash and leached into the quench waters. The DRE calculated on concentration for all PFAS compounds was 93.06% and 95.77% on mass, well below the destruction requirements of the Stockholm and Basel Conventions. The reason for not reaching 99.9999% DRE under normal operating conditions is assumed in the report to be due to a combination of factors including a potential lack of O₂ in the primary chamber, a possible unsuitable/defective injection nozzle and an unsuitable sampling method⁴.

During the *solid waste* burning trial, PFBA and PFPeA were found in the stack emissions, however PFPeA was also found in the blank stack samples. A very high number of PFAS compounds were found in the bottom ash and also leached into the quench waters. Incomplete combustion due to insufficient oxygen was identified as the most likely cause preventing destruction of PFAS compounds in final report⁵. However measured oxygen levels did not fall below 20% (page 9 in the report)⁵, well above the minimum requirement of 10%. Composite sampling of bottom ash was also identified as a better method for assessing average contamination for the trial. Contamination of sampling equipment was shown to be occurring and the use of two different analytical laboratories would likely increase the quality control and accuracy of results. Under normal operating conditions, the incineration of PFAS contaminated activated carbon did not reach the 99.9999% target destruction and removal efficiency (DRE) established for persistent organic pollutants under the Basel and Stockholm Conventions⁵.

Cement kiln PFAS burn trials: DRE for various PFASs ranged from 99.77126 to 99.99993 in cases when the concentration in input waste was measured above level of quantification (LOQ) as summarized in Table 1 below. The laboratory method was not very sensitive for this trial as LOQ for waste of 1 ppm is at the level which is proposed to define the low POPs content level for some PFASs^{8,9}. PFOS, PFOA and PFHxS all had calculated DRE of >99.9999%⁶. Where analytical detection limits did not restrict the calculation of the Destruction and Removal Efficiency calculations (DRE) then PFAS compounds had a calculated DRE >99.99%. (see page 18 in final report)⁶. Relatively low DRE for some of PFASs suggests that significant quantities of PFAS compounds were released to atmosphere. The trial criteria for success was "*full destruction of Fire fighting foam via the main burner and pre-calciner as determined by the destruction efficiency calculation using PFAS analysis results*"¹⁰. On this basis, considering the DRE results for all PFASs measured, the trial was not successful. Although only three groups of PFASs are listed under the Stockholm Convention as yet, undergoing evaluation within EU shows that PFASs should be banned as a class¹¹ and to look only at the DRE levels of PFOS, PFOA and PFH_xS would be a short sighted approach ignoring the precautionary principle mentioned also in the Article 1 of the Stockholm Convention².

The results of PFASs analyses of clinker showed that the content was below detectable limits according the final report by Cement Australia⁶. The detection limit for this analysis under Appendix 3 of the trial report, where the results for clinker were published, was not made publicly available.

Table 1: Mass flow of individual PFAS during trial in cement kiln in Queensland and calculated DRE for them according data provide in the report from Cement Australia⁶. This table provides only data for those PFASs which were measured at levels above LOQ in one of the rates during the trial. Mass Air Emission Rate of 0.00002 g/min was given for measurements below LOQ (<0.000005 mg/m³); see the source for more information⁶.

Individual PFAS Results	Mass Air Emission Rate	Mass Feed Rate In (Volume of PFASs fed to kiln)	Destruction and Removal Efficiency (DRE)
Units	g/min	g/min	%
Perfluorobutanoic acid (PFBA)	0.00002	0.07241	99.97238
Perfluoropentanoic acid (PFPeA)	0.00000079	0.10383	99.99924
Perfluorohexanoic acid (PFHxA)	0.00002	0.46450	99.99569
Perfluoroheptanoic acid (PFHpA)	0.00000039	0.12432	99.99969
Perfluorooctanoic acid (PFOA)	0.00000079	0.31422	99.99975
Perfluoroundecanoic acid (PFUnA)	0.00000079	0.00137	99.94217
Perfluorotridecanoic acid (PFTrDA)	0.00000039	0.00137	99.97145
Perfluorobutanesulfonic acid (PFBS)	0.00002	0.42352	99.99528
Perfluoropentanesulfonic acid (PFPeS)	0.00002	0.42352	99.99528
Perfluorohexanesulfonic acid (PFHxS)	0.00002	3.14224	99.99936
Perfluoroheptanesulfonic acid (PFHpS)	0.00002	0.39620	99.99495
Perfluorooctanesulfonic acid (PFOS)	0.00002	28.55338	99.99993
Perfluorodecanesulfonic acid (PFDS)	0.00002	0.00874	99.77126
1H.1H.2H.2H-perfluorooctanesulfonic acid (6:2 FTS)	0.00002	0.34155	99.99414
1H.1H.2H.2H-perfluorodecanesulfonic acid (8:2 FTS)	0.00002	0.10656	99.98123

Note: For 12 of the 27 PFAS compounds (not listed in table above) measured in the trial, a lower DRE of 98.536 % was calculated based on the levels of input feed as well as concentrations in air emissions below levels of quantification (LOQ), so they might be a result of an insufficiently sensitive analytical method used during the trial – see also table in Appendix 4 p. 1-3 of the Cement Australia report⁶.

4 Discussion

Trials of PFOA and PFOS incineration at the Veolia Dry Creek high temperature hazardous waste incinerator in South Australia (2019) detected some PFAS in emissions but could not calculate a DRE as the concentration of PFAS in the bottom ash following treatment, *was higher than the waste input PFAS concentrations*⁵. This suggests incineration may be a source rather than a sink for PFAS in incineration residues including PFOA and PFOS. The incinerator operators concluded the trial was unsuccessful⁵. For critical evaluation of the trial in the cement kiln in Queensland, Australia important data is missing. The chosen method and detection limits of the PFASs analyses was clearly not sensitive enough and therefore it is hard to evaluate real levels of DE or even DRE for the trial. However, given the main criterion for success of the trial was full destruction of fire-fighting foam as measured by DRE of PFAS analytes, it appears the trial did not successfully achieve its objective. DRE for many of the PFAS compounds was below the required level of 99.9999%.

Municipal waste may contain significant amounts of waste contaminated with PFASs¹² and/or other fluorinated compounds which may lead to PFASs emissions and releases during incineration. PFOS and PFOA were measured in air emissions from waste-to-energy plant in Harlingen, Netherlands¹³. High and/or increased levels of PFASs were also measured by bioassay analyses in mosses and pine needles from the vicinity of two European municipal waste incinerators¹⁴. These results also support suspected generation of PFASs during waste incineration. It has been noted in other studies that flue gases could be a significant source of PFAS emissions from waste incineration plants¹⁵. A study of 31 Swedish incineration plants¹⁶ which measured incineration residuals, but not stack emissions, found PFAS in bottom ash in 9 plants sampled, in fly ash of 15 plants and in condensate water of 13 plants. The study also concluded that PFAS was found irrespective of operating conditions with the highest PFAS levels found in condensate water of incinerators operating above 1100 °C. The authors noted that this occurred “*despite the general hypothesis that all organic substances combust at temperatures above 1000 °C*”¹⁶. This suggests that policy makers should not rely solely on the ‘high temperature’ of combustion facilities as a criterion which will lead to PFAS destruction. The study also found high concentrations of PFAS both in furnaces burning only household waste or only industrial waste suggesting both are a significant source of PFAS.

5 Conclusions

Pilot tests of PFOA and PFOS incineration at the Veolia Dry Creek high temperature hazardous waste incinerator in South Australia (2019) detected some PFAS in emissions but could not calculate a DRE as the concentration of PFAS in the bottom ash following treatment, was higher than the waste input PFAS concentrations. This suggests incineration may be a source rather than a sink for PFAS in incineration residues including PFOA and PFOS. Trial burning of AFFF at the Cement Australia's Fisherman's Landing cement kiln in Gladstone, Queensland (2017) did not reach the minimum target DRE of 99.9999% for many PFAS compounds, suggesting PFAS compounds were released to atmosphere. Comparing this data with the existing literature suggests supports the hypothesis that high temperatures alone are not an accurate predictor of PFAS destruction in combustion facilities. Finally, comparison of the trial burn outcomes with the POPs waste destruction requirement of the Basel and Stockholm conventions suggests that these combustion processes may not be suitable for PFAS waste destruction.

6 Acknowledgements

The study was financially supported by the Government of Sweden through IPEN and the Global Greengrants Fund.

7 References

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