# Experimental Investigation on PFAS Remediation Through Civil Sludge Combustion Processes.

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## Abstract
Incineration process represents a valid solution for Poly-FluoroAlkyl Substances (PFAS) treatment. This study investigates the thermal degradation of sludge containing PFAS and coming from a municipal wastewater treatment plant, by employing a laboratory-scale bubbling fluidized bed combustor operating at 850°C. By utilizing samples of untreated municipal sludge and sludge spiked with a known PFAS mixture, the research could achieve a high analytical sensitivity, enabling a comprehensive evaluation of PFAS combustion efficiency. Preliminary results elucidated the distribution of fluorinated molecules within the combustion byproducts, shedding light on the PFAS degradation pathways during incineration.

## Introduction
The term PFAS (Per- and Poly-FluoroAlkyl Substances) refers to a wide family of organic compounds characterized by partial or complete saturation of carbon atoms with fluorine [**1**]. Normally used in various industrial applications (from paper food packaging to firefighting foams), their stubborn resistance to degradation and their tendency to bioaccumulation and migration has raised concerns about ecological and health threats for human beings. Neurodevelopmental disorders, increased risk of thyroid diseases and cancer risk have been identified as possible outcomes of PFAS exposure [**2**]. PFAS are transferred from the industry to the environment via wastewater treatment plants (WWTP), where PFAS precursors are converted into PFAS mainly via biochemical reactions, e.g., N-ethyl per-fluorooctane sulfonamide (N-EtFOSA) and N-ethyl per-fluorooctane sulfonamidoethanol (N-EtFOSE) are transformed into PFOS (perfluorooctane sulfonate). Alternatively, PFAS originally present in industrial products are released into wastewaters.
High PFAS concentrations have been detected both in wastewater itself and in the sludges produced within the wastewater treatments in different countries like China,

the US and Germany [**1**]. High molecular weight PFAS compounds are less volatile and more hydrophobic, thus they exhibit a strong tendency to adsorb onto sludge matrices reaching concentrations up to thousands of nanograms per gram of dry weight.
In this context, efficient and safe treatment approaches for PFAS removal from municipal sludge is of outstanding importance to limit their spread into the environment. Up to date, different technologies have been studied for PFAS remediation, among which physical (adsorption), thermochemical and biochemical routes **[1].** Incineration of municipal sludges at high temperatures (800-900°C) is one of the possible strategies studied to degrade PFAS molecules [3], but more research is needed on the fate of PFAS compounds, on the degradation efficiency and on the fluorinate molecules distribution within the combustion flue gas and the ash. In this work, results from a preliminary experimental campaign of municipal sludge combustion are presented. PFAS thermal degradation during sludge incineration has been studied using a laboratory-scale bubbling fluidized bed combustor operated at 850°C and atmospheric pressure.

## Materials and methods

Different combustion tests were performed using a laboratory scale bubbling fluidized bed combustor (40 mm ID and 1 m height) at a constant temperature of 850°C and a fluidization velocity of 0.5 m/s. The residence time was 2 s. Silica sand (300-400 μm) has been used as bed material. A metallic filter, kept at 300°C to avoid vapor condensation, was used to collect elutriated particles. A schematic representation of the experimental setup is reported in Figure 1.

The fuel (sludge) was continuously fed through a mechanical-pneumatic system consisting of a loading hopper positioned on a screw feeder that transports the solid particles into a little jar into which a flow of air pneumatically injects the particles at the base of the bed. For this reason, the fuel was crushed and sieved to small particles (<1 mm). During each experimental run, the fuel feeding rate was adjusted to have a stable oxygen concentration of 4-6% in the flue gas. Proximate and ultimate analyses were performed according to ASTM and UNI standards using a LECO TG701 thermogravimetric balance (ASTM D5142), LECO CS144 (ASTM D 4239) and a LECO CHN 628 elemental analyzer (ASTM D5373), respectively. The calorific value was determined using a PARR 6200 calorimeter (ASTM D 5865) with a Mahler calorimeter bomb. Metal analyses were performed by ICP-MS (Agilent 7500CE) after dissolution of the samples by microwave-assisted acid digestion, in accordance with US-EPA Methods 3051 and 3052. All measurements were repeated at least three times. Flue gas analysis has been performed online for $O_2$, CO, $CO_2$, and $NO_x$ concentration.

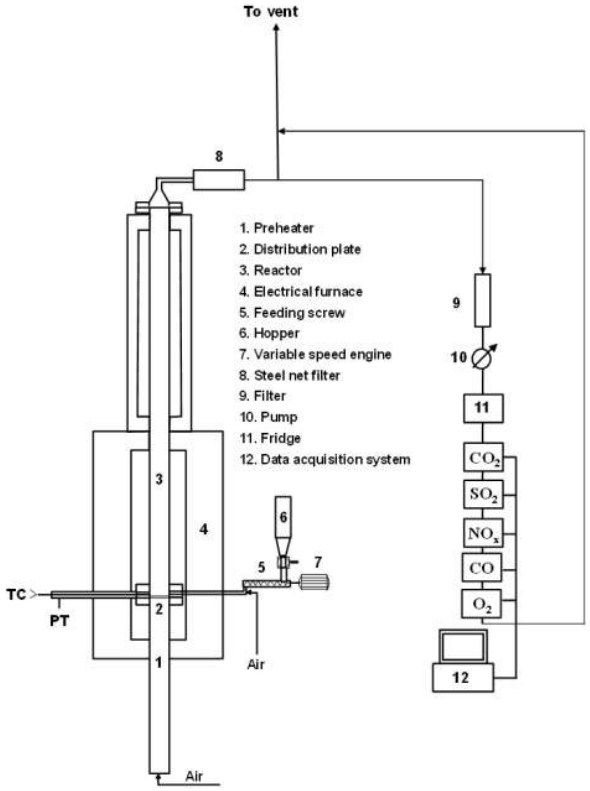


**Figure 1.** Laboratory scale fluidized bed combustor used in the experimental campaign.

Sampling and analysis of PFAS has been conducted by an external laboratory, which employed specific advanced techniques for high resolution evaluation of these contaminants. To assess the efficiency of PFAS destruction in the incineration process, the sludge was spiked with known amounts of 5 representative PFAS compounds, as shown in Table 1. The PFAS enrichment of the sludge was necessary, given the low concentrations of PFAS present in the actual starting sludge, to allow adequate analytical sensitivity. Spiked sludge samples exhibited PFAS concentrations surpassing those found in raw sludge by a factor of 100.

**Table 1.** PFAS content in spiked sludge.

| **Compound** | **Sludge 1[mg/kg]** | **Sludge 2[mg/kg]** |
|---|---|---|
| PFBS | 1.9 | 0.2 |
| PFTeDA | 1.8 | 0.5 |
| PFOA | 1.9 | 1.7 |
| PFBA | 2.0 | 2.4 |
| PFOS | 1.0 | 0.9 |
| Total PFAS | 8.5 | 5.8 |

The representative characteristics of the dry sludge used in the experimental campaign are reported in Table 2. The ICP analysis shows high concentration of some elements, especially Fe (~4%wt.), P (~3%wt.) and Ca (~2%wt.).

**Table 2.** Proximate and ultimate analyses of the sludge samples (as received, %wt).

| **Analysis** | **Sludge 1** | **Sludge 2** |
|---|---|---|
| Moisture | 4.7 | 4.5 |
| Volatiles | 65.3 | 61.3 |
| Fixed carbon | 8.1 | 4.9 |
| Ash | 21.9 | 29.4 |
| Carbon | 36.2 | 31.6 |
| Hydrogen | 5.4 | 4.6 |
| Nitrogen | 5.7 | 6.1 |
| Sulfur | 0.98 | 0.96 |
| Clorine | 0.12 | 0.075 |
| Fluorine | 0.018 | 0.0112 |
| Oxygen (by difference) | 25.0 | 22.8 |
| LHV [kJ/kg] | 15139 | 13457 |

Table 3 illustrates the experimental conditions of the combustion tests, particularly referring to the fuel feed rate and excess of combustion air.

**Table 3.** Operating conditions for the experimental tests.

| **Name** | **N°1** | **N°2** | **N°3** | **N°4** | **N°5** | **N°6** | **N°7** | **N°8** |
|---|---|---|---|---|---|---|---|---|
| Feed, g/h | 119.7 | 115.5 | 126.8 | 113.2 | 103.6 | 101.1 | 103.4 | 99.3 |
| Power, $kW_{th}$ | 0.491 | 0.474 | 0.533 | 0.476 | 0.387 | 0.378 | 0.386 | 0.371 |
| Air excess, % | 18 | 22 | 12 | 26 | 58 | 62 | 58 | 65 |

## Results and discussion

Tests from N°1 to N°4 were performed using a lower excess air (20-30%) compared to tests N°5 to N°8 (50-60%). This difference significantly influenced the efficiency of the combustion process in terms of pollutant emissions and ashes recovery from the combustor. From Table 4 it can be noted that higher $O_2$ content in the reactor lead to a reduction in CO and $NO_x$ production from 2500-3000 ppm to 1100-1300 ppm and from 2500-3200 ppm to 1000-1600 ppm respectively. A more complete combustion is achieved when oxygen is in large excess, reaching a 99% combustion

efficiency. The fly ash concentration and their carbon content are comparable to values obtained in other experiments [4].

**Table 4.** Main results from the sludge incineration tests.

| Name | N°1 | N°2 | N°3 | N°4 | N°5 | N°6 | N°7 | N°8 |
|---|---|---|---|---|---|---|---|---|
| | | | | | | | | |
| Testing time, h | 4 | 4 | 4 | 4 | 2 | 2 | 4 | 4 |
| Combustion efficiency, % | 96.4 | 96.3 | 96.3 | 95.5 | 98.94 | 98.96 | 99.02 | 98.86 |
| **Mean composition of flue gas v/v.** | | | | | | | | |
| $O_2$, % | 3.89 | 4.07 | 4.21 | 4.88 | 7.37 | 6.39 | 6.79 | 6.95 |
| $CO_2$, % | 14.19 | 13.98 | 14.32 | 13.27 | 11.14 | 12.00 | 11.72 | 11.56 |
| CO, ppm | 2801 | 2871 | 2506 | 2614 | 1178 | 1243 | 1122 | 1306 |
| $NO_x$, ppm | 2900 | 3200 | 2500 | 2700 | 1000 | 1174 | 1487 | 1608 |
| **Flowrate and concentration of ash** | | | | | | | | |
| Fly ash, g/h | 10.10 | 10.74 | 14.57 | 10.84 | 4.8 | 5.93 | 8.55 | 8.03 |
| Carbon in Fly ash, g/h | 0.019 | 0.03 | 0.168 | 0.146 | 0.006 | 0.007 | 0.01 | 0.01 |
| Fly Ash concentration, mg/Nm$^3$ | 17451 | 18519 | 25123 | 18686 | 8266 | 10220 | 14742 | 13845 |
| Bottom ash, g/h | 17.3 | 17.0 | 10.7 | 13.4 | 23.1 | 19.3 | 21.1 | 22.6 |

Results from the experimental campaign suggest that the mean PFAS abatement efficiency was from 99.95 to 99.97%. The analysis conducted on the flue gas revealed the presence of only PFBS with a concentration of 10.6-37.2 ng/Nm$^3$ when the $O_2$ excess was lower (tests N°1 to N°4), while both PFOS and PFTeDA were detected with a mean concentration of 4.0 and 6.5 ng/Nm$^3$ during the other tests. In summary, in the exhaust gases only 3 out of 5 compounds were not eliminated by the incineration process in the fluidized bed combustor but the concentration was reduced by 6 orders of magnitude compared to the initial one. As for the residual ash from the combustion process, PFAS concentrations ranged from 200-600 ng/kg in the bottom ashes to 3000-24000 ng/kg in the fly ashes.

## Conclusions

Incineration of municipal sludge samples spiked with a known amount of 5 different PFAS compounds was performed using a fluidized bubbling bed combustor operated at 850°C. The experimental campaign aimed to assess the efficacy of the combustion process for the abatement of persistent PFAS compounds. Some preliminary results showed that the mean PFAS destruction in the incineration process was always greater than 99.9%. Only PFBS, PFOS ad PFTeDA were detected in the flue gas with a concentration of 4-10 ng/Nm$^3$, while a PFAS concentration in the order of 200 – 24000 ng/kg was detected in the residual ashes.

## References

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