Task ID**:** 425.015

Task Title**:** Reductive Dehalogenation of Perfluoroalkyl Surfactants in Semiconductor Effluents.

Deliverable**:** Report on the susceptibility of PFOS and related perfluoroalkyl surfactants to microbial reductive dehalogenation.

Summary Abstract:

Perfluorooctane sulfonate (PFOS) and related perfluorinated alkyl surfactants (PFAS) are emerging contaminants which find important applications in photolithography operations of semiconductor manufacturing. Although more environmentally benign chemistries are under development, commercial alternatives to PFOS for critical photolithography uses are still lacking. Therefore, the development of treatment techniques to decompose PFOS is crucial to reduce and eliminate the environmental release of this ubiquitous pollutant. Treatment of PFOS in wastewater is challenging due to the outstanding resistance of this surfactant against chemical and biological degradation.

Reductive dehalogenation is an important mechanism contributing to the biodegradation of highly halogenated compounds previously thought to be recalcitrant such as polychlorinated biphenyl (PCBs) and polybrominated diphenylethers (PBDEs) *(1)*. Although microbial degradation of various organofluorines compounds is well documented *(2)*, no studies have been published to date considering the biological reductive defluorination of PFOS and related perfluoroalkyl surfactants.

The main objective of the research reported here is to investigate the feasibility of microbial reductive dehalogenation for the removal of PFOS and related long chain perfluorinated compounds in semiconductor effluents. The results of this study indicate that perfluorinated alkyl surfactants are highly resistant to microbial degradation and that these compounds are not reductively dehalogenated even after very long periods of incubation (18-24 months). PFOS-related compounds with a shorter alkyl chain (e.g., perfluorobutane sulfonate or PFBS) and partially defluorinated PFOS molecules (e.g., TH-PFOS) were also resistant to biodegradation.

Technical Results and Data:

Microbial degradation of PFOS and several related fluorinated compounds including, perfluorobutane sulfonate (PFBS, a fluorinated derivative proposed as an environmentally-benign alternative to PFOS), TH-PFOS (*H*,1*H*,2*H*,2*H*-perfluorooctane sulfonic acid or $C_6F_{13}C_2H_4SO_3H$, a partially defluorinated PFOS-derivative, and perfluorooctanoic acid (PFOA), was evaluated in anaerobic shaken batch bioassays. The experiments were inoculated with sediments or sludge samples obtained from a variety of sources, including inocula previously exposed to fluorinated compounds (e.g. biosolids from wastewater treatment plants receiving PFOS-containing semiconductor wastewaters). H_2 gas was supplied as primary electron-donating substrate for the halorespiring microorganisms and it was replenished periodically by flushing the headspace of the bioassays with H_2/CO_2 gas (80/20, v/v). Sludge controls (no fluorinated compound added) and abiotic controls (microorganisms killed by autoclaving) were run in parallel to determine background fluoride concentrations and to account for the loss of fluorinated compounds by mechanisms other than microbial dehalogenation (e.g., surfactant removal by sorption to the biomass). Assessment of reductive dehalogenation relied on the monitoring of fluoride release using an ion-selective electrode. Samples of the culture medium were also withdrawn periodically for the analysis of fluorinated compounds by ion chromatography with suppressed conductivity detection. Samples of the headspace were

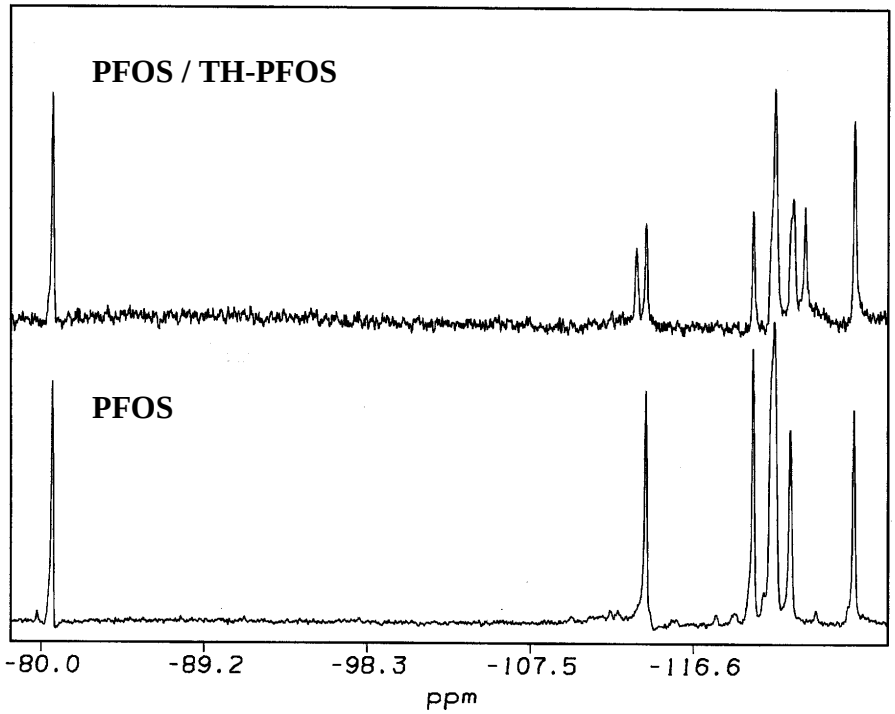

Fig. 1. *F-NMR spectra of solutions containing perfluorooctane sulfonate (PFOS) / tetrahydro-PFOS (TH-PFOS) at 1:1 molar ratio and PFOS alone. The peak at -80 ppm can be assigned to the internal standard.*

analyzed by GC-MS to examine the possible formation of volatile fluorinated metabolites. Selected liquid samples were also investigated using ^{19}F-nuclear magnetic resonance (F-NMR, Fig. 1) and liquid chromatography tandem mass spectrometry (LC/MS-MS), two different techniques which can serve, respectively, to detect changes in the fluorine substitution pattern and to identify putative microbial metabolites of the parent compounds.

The highly oxidized character of perfluorinated compounds is expected to make them more prone to microbial attack in anaerobic reducing environments as compared to aerobic conditions. Nonetheless, no evidence has been obtained that the perfluorinated compounds assayed are biodegraded by any of the inocula tested after more than 18 to 24 months of incubation under anaerobic conditions. These results appear to confirm the outstanding resistance of PFOS and other perfluorinated compounds to microbial attack. It is interesting to note that TH-PFOS, a partially defluorinated PFOS derivative, was not degraded in our experiments. TH-PFOS was reported to be biodegradable in previous studies conducted under aerobic conditions *(3)*.

Technical PFOS is a mixture of linear and branched structural isomers, with the latter making up 20 to 30% of the total mass. Work conducted in the frame of this study has shown that branched PFOS isomers are more susceptible to biomimetic reductive dehalogenation than the linear PFOS isomer *(4)*. These results suggest that branching may facilitate the microbial degradation of perfluorinated compounds. Future efforts will assess the microbial transformation of branched PFOS isomers in anaerobic environments.

References:

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4. **Ochoa-Herrera, V. et al.** 2008. Reductive defluorination of perfluorooctane sulfonate. *Environ. Sci. Technol.* **42**, 3260-3264