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 chemical biomimetic degradation.

Summary Abstract:

Perfluoroctane sulfonate (PFOS, $C_8F_{17}SO_3H$) and related perfluorinated alkyl surfactants (PFAS) are essential components in semiconductor manufacturing. These fluorinated chemicals are utilized as photoacid generators in photolithography, and they are components of antireflective coatings and surfactant formulations. Removal of perfluorinated compounds from semiconductor effluents utilizing conventional physico-chemical and biological methods is limited by technical and economic considerations. Therefore, there is an urgent need for feasible methods to remove PFOS/PFAS from semiconductor effluents in order to minimize environmental release of these emerging pollutants.

The objective of the work presented here is to investigate the feasibility of biomimetic reductive dehalogenation for the destruction of PFOS and related perfluoroalkyl surfactants in semiconductor wastewaters. Reductive dehalogenation is an important mechanism contributing to the biodegradation of highly chlorinated compounds *(1)*. Most known reductive dehalogenases are dependent on the corrinoid cofactor, vitamin B_{12} (cyanocobalamin). This cobalt-containing cofactor catalyzes reductive dehalogenation *in vitro* when supplied with an appropriate reducing agent such as titanium (III) (*2*). The direct catalysis of dehalogenation by enzyme cofactors is known as *biomimetic dehalogenation*, because it mimics reactions expected in microorganisms.

Technical Results and Data:

Our results has demonstrated that PFOS can be defluorinated by biomimetic reduction with vitamin B_{12} (260 µM) as catalyst and Ti(III)-citrate (36 mM) as bulk reductant in anoxic aqueous solution at 70°C and pH 9.0. This finding is highly significant because it is the first report of reductive dehalogenation of PFOS. Reduction of technical PFOS was confirmed by measuring the release of fluoride ions, which accounted for 18% of the initial fluorine content in less than one week. The fluoride released was equivalent to the removal of three fluorine atoms per mol of PFOS. ^{19}F-NMR of the aqueous phase confirmed the presence of inorganic fluoride ions. Defluorination was also observed at ambient conditions (30°C, pH 7.0) albeit at considerably lower rates. No significant reduction of PFOS was observed in the absence of either vitamin B_{12} or Ti(III) citrate, nor in controls in which vitamin B_{12} was replaced with cobalt (II) or in controls with Ti(IV) in lieu of Ti(III)-citrate.

Fig. 1 illustrates the proposed mechanism of biomimetic reductive dehalogenation of PFOS with vitamin B_{12} / Ti(III) citrate.

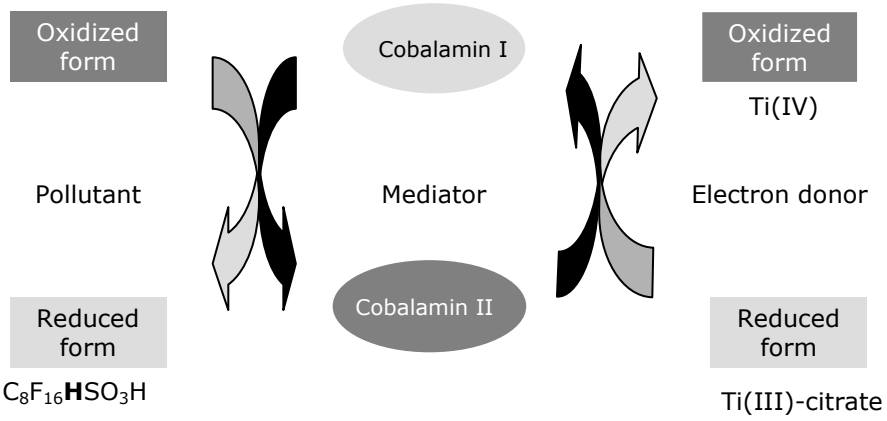

Fig. 1. *Proposed mechanism of biomimetic reductive dehalogenation of PFOS with vitamin B_{12} / Ti(III).*

The impact of vitamin B_{12} and Ti(III) citrate dosage, pH and temperature was assessed to determine the optimal treatment conditions. The rate of PFOS degradation increased 37-fold with increasing temperature from 30º to 70ºC. Increase of the reaction pH from 7.5 to 9.0 also had a positive impact on the rate of PFOS defluorination, although less marked compared to the results obtained at high temperature (5.9-fold enhancement in the rate of dehalogenation).

Monitoring of PFOS degradation by suppressed conductivity ion chromatography revealed that PFOS isomers differed in their susceptibility to reductive degradation by vitamin B_{12}/Ti(III) citrate. Chromatographic peaks corresponding to branched PFOS isomers disappeared whereas the peak corresponding to linear PFOS was stable. Technical PFOS used by industry is a mixture of linear and branched structural isomers (Fig. 2), with the latter making up 20 to 30% of the total mass. ^{19}F-NMR and LC-MS/MS studies revealed that the PFOS material used in this study contained 24.6% branched isomers, consisting chiefly of the following perfluoromonomethyl isomers: 3-CF_3-PFOS and 4-CF_3- PFOS (peak I in LC-MS/MS trace, Fig. 3A), 5-CF_3-PFOS and 6-CF_3- PFOS (peak II), and 1-CF_3- PFOS (peak III). The branched PFOS isomers were purified and assessed for reductive dehalogenation by vitamin B_{12} at 70°C, pH 9.0. The susceptibility of the branched PFOS isomers to reductive dehalogenation was confirmed by fluoride release measurements (71% of the initial fluorine was released after 5 days) as well as by ion chromatography, LC-MS/MS and F-NMR studies (Figs. 3 and 4). The degradation of branched PFOS isomers followed pseudo-first-order kinetics with a rate constant of 0.49 d^{-1}. The LC-MS/MS chromatograms indicate removal of the isomers, 5- and 6-CF_3- PFOS by 80 $\pm$ 1%, 3- and 4-CF_3- PFOS by 48 $\pm$ 1%, and 1-CF_3- PFOS by 44 $\pm$ 2%. Isomer degradation was confirmed

by the nearly complete disappearance of the signal corresponding to the branched CF_3 group and other organic fluorine signatures characteristic of the branched PFOS structures in ^{19}F-NMR spectra (Fig. 4B).

The reaction mechanism of vitamin B_{12}-catalyzed reductive dehalogenation is poorly understood. The most commonly accepted models for highly chlorinated hydrocarbons hypothesize that the attack involves radical intermediates. Electron paramagnetic resonance (EPR) measurements conducted in this study have confirmed the formation of a vitamin B_{12} carbon-centered radical. The enhanced susceptibility of branched PFOS isomers to reductive dehalogenation might be related to the stabilizing effect of branched structures on radical intermediates resulting from the reductive attack. Also, steric hindrance caused by $–CF_3$ groups decreases the strength of the C─C bond in branched perfluoroalkanes.

To our knowledge this is the first report of reductive dehalogenation of PFOS catalyzed by a biomolecule. These results suggest that microbial transformation of some PFOS isomers might be possible in anaerobic environments. Furthermore, the observation that branched PFOS isomers are more prone to attack than linear PFOS provide clues for the design of more biodegradable perfluorinated chemicals.

References

1. **Smidt & de Vos.** Anaerobic microbial dehalogenation. *Annu. Rev. Microbiol.* **58**, 43-73 (2004).
2. **Banerjee & Ragsdale.** The many faces of vitamin B12: Catalysis by cobalamin-dependent enzymes. *Annu. Rev. Biochem.* **72**, 209-247 (2003).

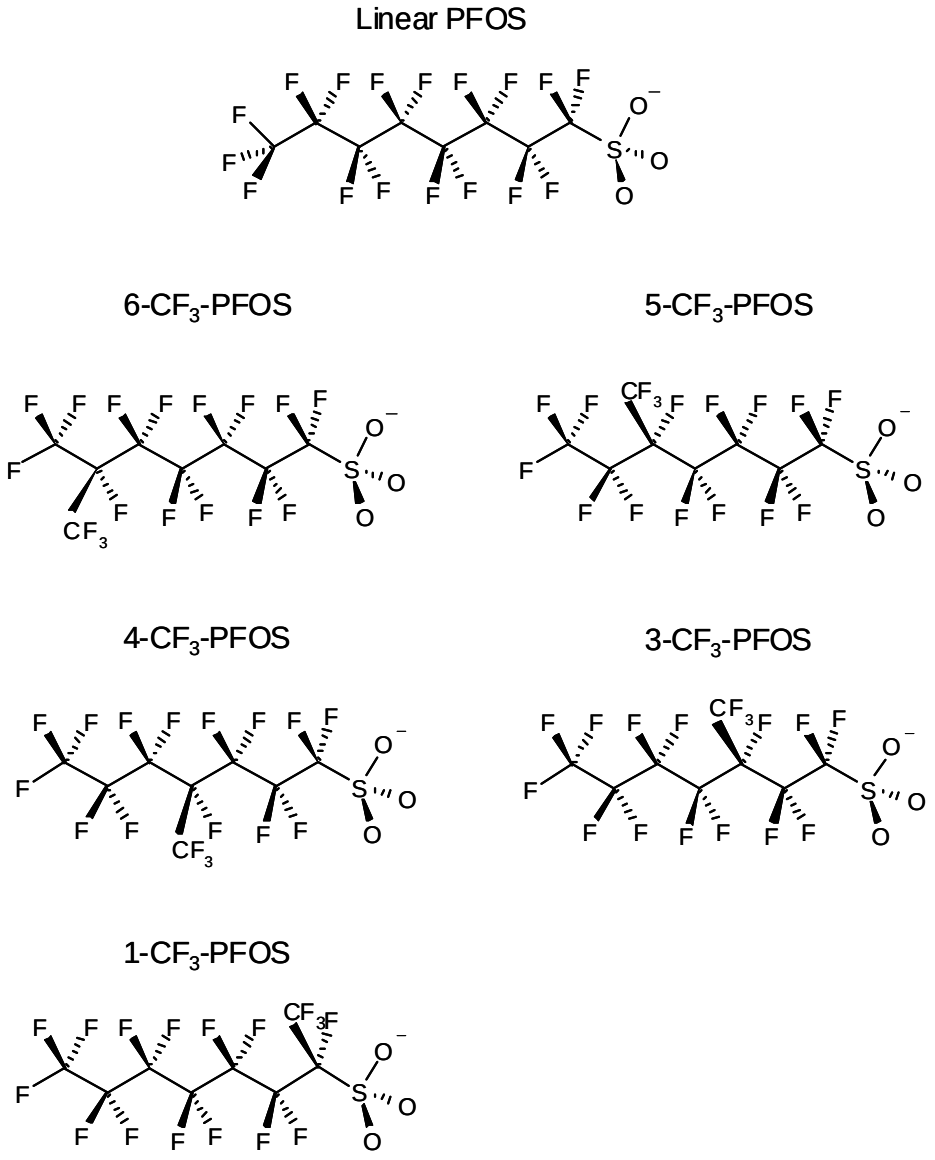

Fig. 2. Chemical structure of linear- and branched PFOS isomers: 6-perfluoromethyl-PFOS (6-CF_3-PFOS), 5-perfluoromethyl-PFOS (5-CF_3-PFOS), 4-perfluoromethyl-PFOS (4-CF_3-PFOS), 3-perfluoromethyl-PFOS (3-CF_3-PFOS) and 1-perfluoromethyl-PFOS (1-CF_3-PFOS).

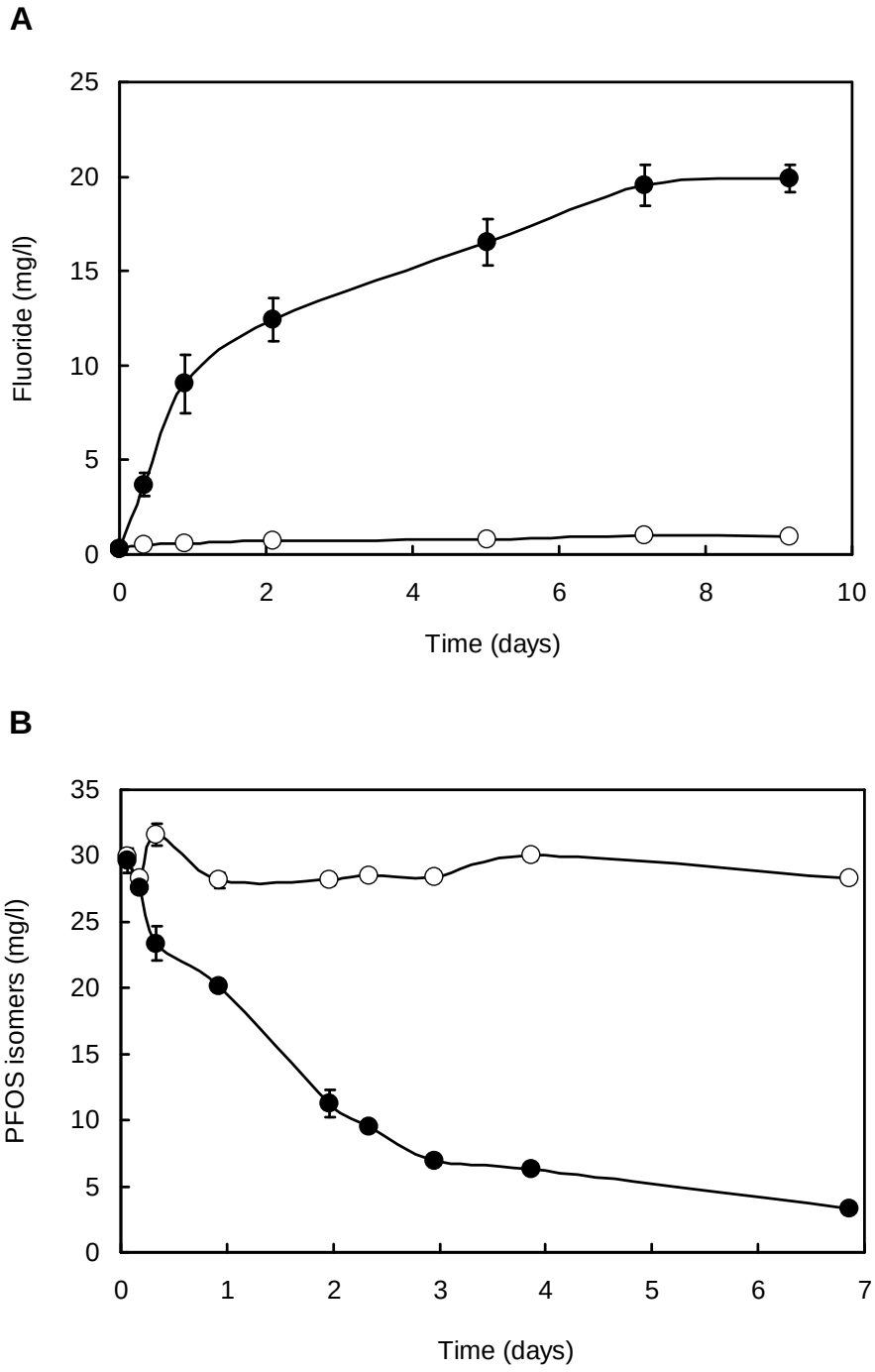

Fig. 3. Biomimetic reductive dehalogenation of technical PFOS with vitamin B12 (260 µM) and Ti(III) citrate (36 mM) in control samples (PFOS + Ti(III) citrate) and treatment samples (PFOS + Ti(III) citrate + vitamin B_{12}). **(A)** Time course of fluoride release of technical PFOS monitored using an ion selective electrode in control samples (○) and treatment samples (●). **(B)** Time course disappearance of branched PFOS isomers based on suppressed conductivity ion chromatography analysis in control samples (○) and treatment samples (●). Error bars (shown if larger that the symbols) represent standard deviations of triplicate assays. Samples were incubated at 70ºC and pH 9.0 for 7 days.

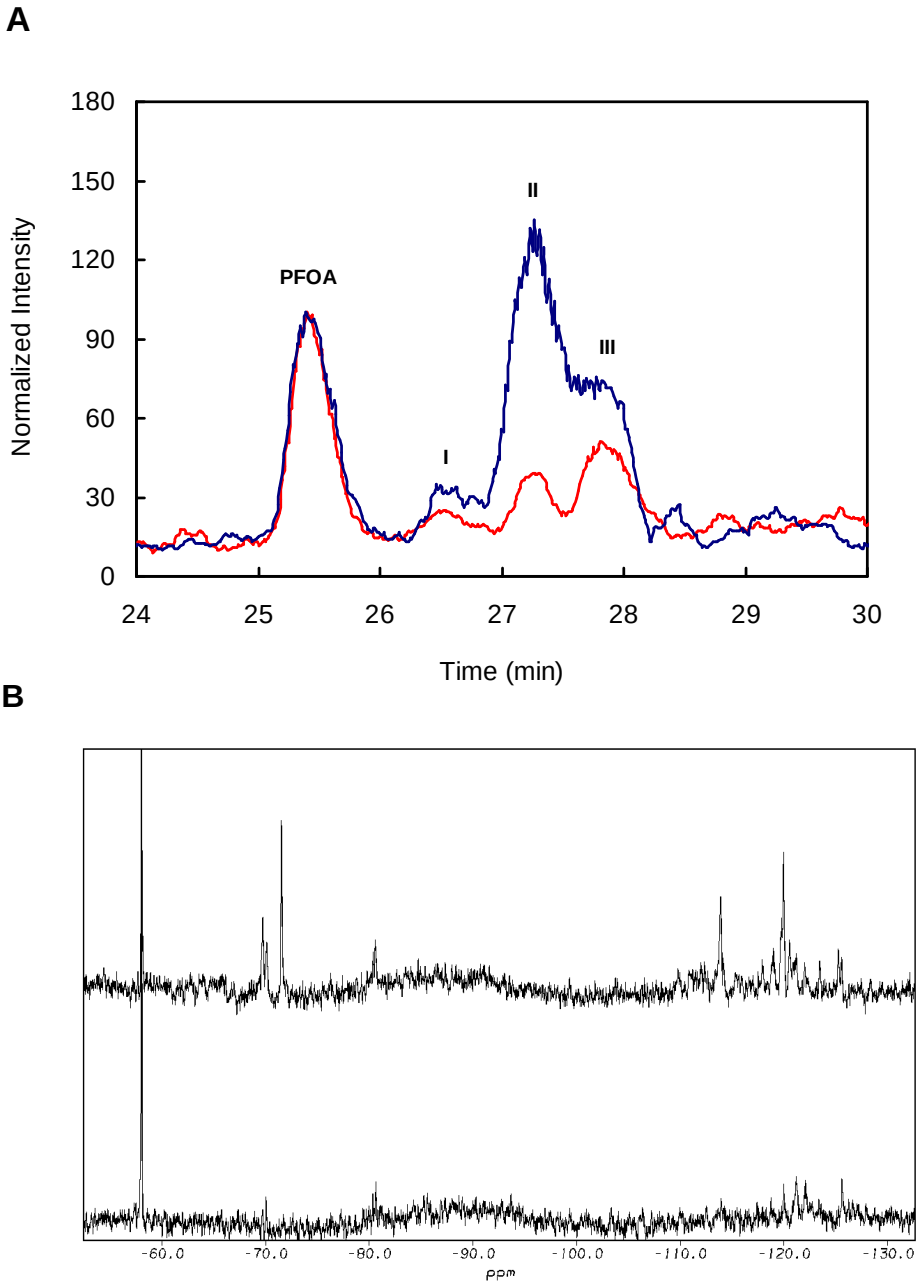

Fig. 4. Biomimetic reductive dehalogenation of technical PFOS with vitamin B12 (260 µM) and Ti(III) citrate (36 mM) in control samples (PFOS + Ti(III) citrate) and treatment samples (PFOS + Ti(III) citrate + vitamin B_{12}). **(A)** LC-MS/MS chromatograms of branched PFOS isomers in control samples (*blue*) and treatment samples (*red*). PFOA (perfluorooctanoic acid) was the internal standard. **(B)** ^{19}F-NMR spectra of branched PFOS isomers in control (upper panel) and treatment samples (lower panel). Samples were incubated at 70ºC and pH 9.0 for 7 days.