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) 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. 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. Removal of perfluorinated compounds from semiconductor effluents utilizing conventional physico-chemical and biological methods is limited by technical and economic considerations.

The objective of this study is to investigate the feasibility of biomimetic reductive dehalogenation with vitamin B_{12} and Ti(III)-citrate 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 (Smidt & de Vos, 2004). 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) (Banerjee & Ragsdale, 2003). The direct catalysis of dehalogenation by enzyme cofactors is known as *biomimetic dehalogenation*, because it mimics reactions expected in microorganisms.

Our results has demonstrated that PFOS can be defluorinated by biomimetic reduction with vitamin B_{12} as catalyst and Ti(III)-citrate as bulk reductant in anoxic aqueous solution at 70°C and pH 9.0 (Ochoa-Herrera *et al.* 2008). Furthermore, they indicate that branched PFOS isomers are more prone to degradation than linear isomers. 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. The observation that branched PFOS isomers are more prone to attack than linear PFOS also provides clues for the design of more biodegradable perfluorinated chemicals.

The mechanism involved in the reductive dehalogenation of PFOS is unknown. Electron paramagnetic resonance (EPR) measurements demonstrated the formation of a vitamin B_{12} carbon-center radical in the presence of a strong electron donor such as Ti(III) citrate. This radical intermediate presumably initiates the reductive dehalogenation of PFOS. LC-MS/MS, solid and liquid ^{19}F-NMR and GC/MS studies were conducted to identify the products of the biomimetic reductive dehalogenation of PFOS. No PFOS degradation products other than

fluoride were detected either in the reaction solution after treatment with vitamin B_{12} and Ti(III) citrate. Small quantities of fluorinated hydrocarbons were detected in the gas phase.

Experimental conditions optimizing PFOS reductive dehalogenation were determined. The rate of PFOS defluorination increased significantly with increasing temperature from 30º to 70ºC, and the reaction pH from 7.5 to 9.0. Under those conditions, the optimum dosage of vitamin B_{12} and Ti(III) citrate were 262-545 μM and 57 mol Ti(III)/mol PFOS, respectively.

Vitamin B_{12} can be immobilized onto faujasite zeolite to facilitate the continuous-flow treatment of wastewaters contaminated with PFOS and related perfluorinated compounds using biomimetic reductive dehalogenation.

Technical Results and Data:

Our results have demonstrated that PFOS can be defluorinated by biomimetic reduction with vitamin B_{12} as catalyst and Ti(III)-citrate as bulk reductant in anoxic aqueous solution at 70°C and pH 9.0 (Ochoa-Herrera *et al.* 2008). 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. ^{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.

Vitamin B_{12} is a cobalt-containing molecule. The effectiveness of cobalt (II) in lieu of vitamin B_{12} in catalyzing the reduction of technical PFOS was evaluated under optimized treatment conditions of temperature and solution pH (70ºC and 9.0). No significant reduction of PFOS was observed in treatment samples containing cobalt (II) at concentrations up to 20-fold greater than those present in the assays amended with vitamin B_{12}. These results confirm that the biomolecule is responsible for the dehalogenation of PFOS.

Monitoring of PFOS degradation by suppressed conductivity ion chromatography (IC) 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. 1), 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% initial fluorine released

after 5 d) as well as by IC, LC-MS/MS and F-NMR studies (Fig. 2). The fluoride released was equivalent to the removal of twelve fluorine atoms per mol of PFOS degraded. The degradation of branched PFOS isomers followed pseudo-first-order kinetics with a rate constant of 0.49 d^{-1}. LC-MS/MS results showed removal of the isomers, 5- and 6-CF_3- PFOS by 80%, 3- and 4-CF_3- PFOS by 48%, and 1-CF_3- PFOS by 44%. Isomer degradation was confirmed by the nearly complete disappearance of the signal corresponding to the branched CF_3 group and other organic fluorine signatures distinctive of the branched PFOS structures in ^{19}F-NMR spectra (Fig. 3). These spectroscopic signals have been characterized and assigned for the individual branched PFOS isomers elsewhere (Arsenault et al. 2005).

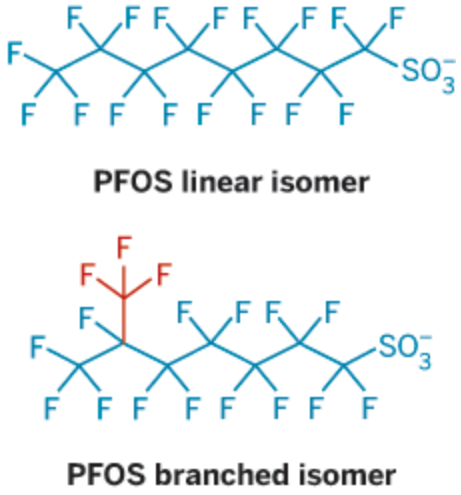

Fig. 1. *Chemical structure of linear- and branched PFOS isomers.*

The reaction mechanism involved in the 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.

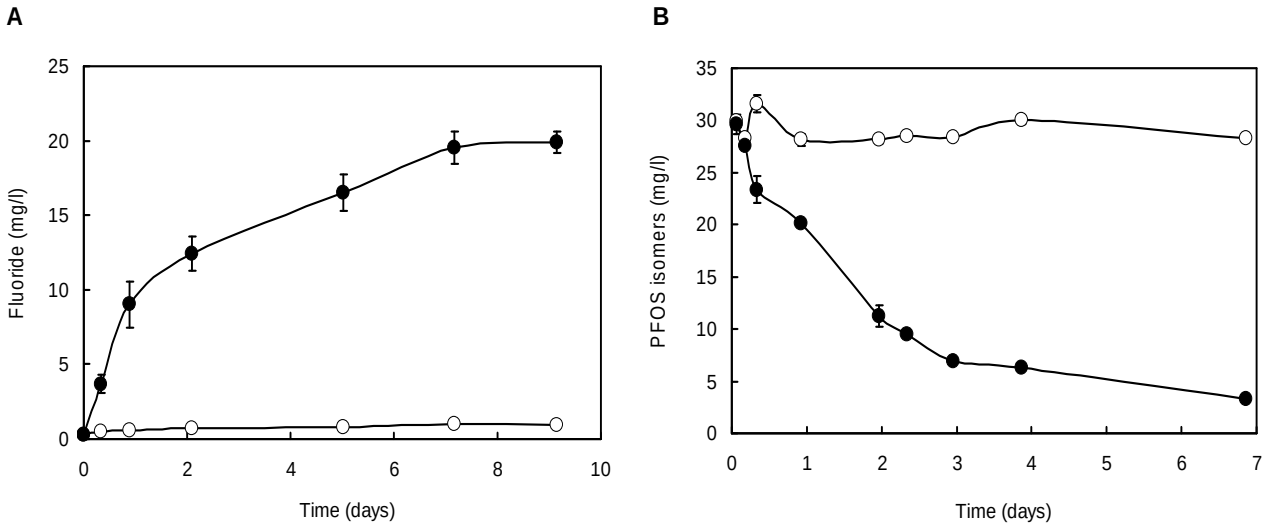

Fig. 2. *Biomimetic reductive dehalogenation of technical PFOS with vitamin B12 (260 µM) and Ti(III) citrate (36 mM) in control samples (PFOS + Ti(III) citrate) and treatment samples (PFOS + Ti(III) citrate + vitamin B_{12}).* ***(A)*** *Time course of fluoride release of technical PFOS monitored using 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.*

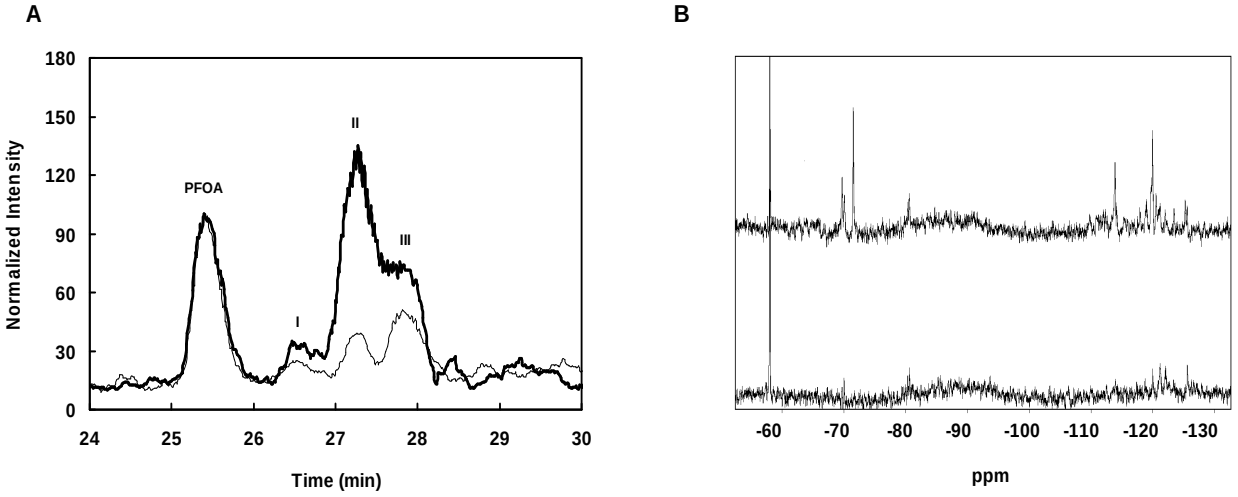

Fig. 3. *Biomimetic reductive dehalogenation of branched PFOS isomers at 70ºC and pH 9.0 at day 7. (A) LC-MS/MS chromatograms of branched PFOS isomers in control samples (PFOS + Ti(III) citrate) (thick line) and treatment samples (PFOS + Ti(III) citrate + Vitamin B_{12}) (thin line). (B) ^{19}F-NMR spectra of branched PFOS isomers in control (upper panel) and treatment samples (lower panel).*

LC-MS/MS, solid and liquid ^{19}F-NMR and GC/MS studies were conducted to identify the products of the biomimetic reductive dehalogenation of PFOS. No PFOS degradation products were detected in the reaction solution after treatment with vitamin B_{12} and Ti(III) citrate. The insoluble/colloidal materials present in the reaction mixture were also analyzed. Solid-liquid extractions of the precipitate were performed with different solvents, methanol, acetonitrile, dimethyl sulfoxide (DMSO), hexane and ethyl ether. LC-MS/MS and ^{19}F-NMR analysis of the extract revealed only the presence of linear PFOS; no signs of PFOS-derivatives or other fluorinated compound were obtained. Interestingly, small amounts of volatile fluorinated compounds, representing less than 10% of the PFOS degraded, were detected in the headspace of the reaction flasks using GC-MS. Those included perfluorinated as well as partially fluorinated hydrocarbons (Fig. 4). These results indicate that although the PFOS molecule is highly defluorinated by the biomimetic treatment (12 mol F^- released/mol branched PFOS in 5 days), small fractions of the PFOS molecule appear to undergo cleavage of the sulfonic group, resulting in the formation of volatile degradation products.

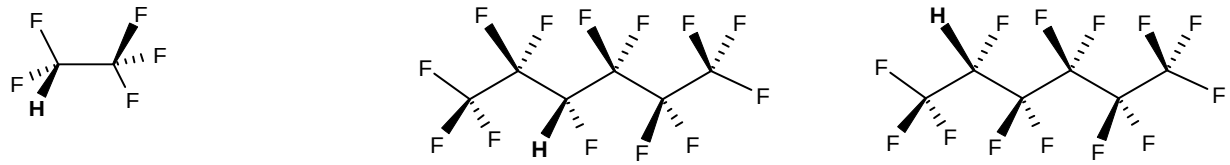

Fig. 4. *Tentative chemical structure of the volatile fluorinated compounds detected in the headspace of reaction flasks following reductive dehalogenation of PFOS with vitamin B12 and Ti(III) citrate.*

Experimental conditions for optimizing PFOS reductive dehalogenation were determined, in particular, reaction temperature, reaction pH, as well as vitamin B_{12} and Ti(III)-citrate dosage. The rate of PFOS defluorination increased significantly with increasing temperature from 30º to 70ºC, and the reaction pH from 7.5 to 9.0. Under those conditions, the optimum dosage of vitamin B_{12} and Ti(III) citrate were 262-545 μM and 57 mol Ti(III)/mol PFOS, respectively (Fig. 5).

Immobilization of vitamin B_{12} on solid supports such as activated carbon (F400, Calgon Carbon Corporation) and zeolite (NaY80, Zeolyst Int.) was investigated to facilitate continuous treatment. Faujasite zeolite had a moderate positive impact on the rate of PFOS defluorination (1.4-fold increase in the reaction rate at 70ºC, pH 9.0). These results indicate that faujasite zeolite could be utilized in continuous-flow reductive dehalogenation processes as an effective sorbent for the immobilization of the catalyst.

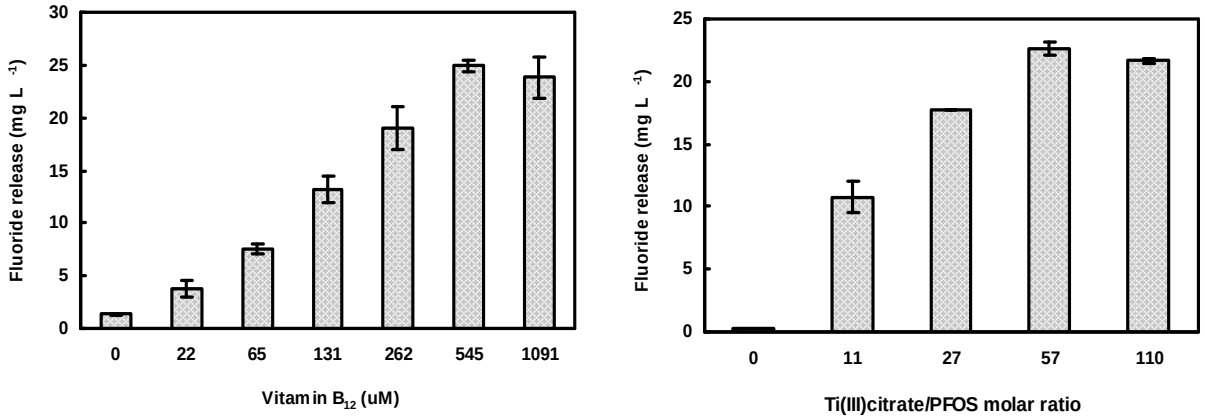

Fig. 5. Effect of vitamin B_{12} concentrations (top panel) and Ti(III) citrate/PFOS molar ratio (lower panel) on the biomimetic reductive dehalogenation of PFOS at day 3 at 70ºC. Control samples (PFOS + Ti(III) citrate) and treatment samples (PFOS + Ti(III) citrate + vitamin B_{12}).

References:

1. **Smidt & de Vos.** 2004. Anaerobic microbial dehalogenation. *Annu. Rev. Microbiol.* **58**, 43-73.
2. **Banerjee & Ragsdale.** 2003. The many faces of vitamin B12: Catalysis by cobalamin-dependent enzymes. *Annu. Rev. Biochem.* **72**, 209-247.
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4. **Arsenault, G., et al.**, 2005. Separation and fluorine nuclear magnetic resonance spectroscopy (^{19}F-NMR) analysis of the individual branched isomers present in technical perfluorooctanesulfonic acid (PFOS). *Organohal. Compounds.* **67,** 818-822.