

Nucleophilic Substitution Reactions in Hydrothermal Degradation of Per- and Polyfluoroalkyl Substances

Objectives

- Investigate the importance of nucleophilic substitution reactions in degrading per- and polyfluoroalkyl substances (PFAS) during hydrothermal treatment
 - Specific focus on degradation of ultrashort chain trifluoromethane sulfonate (TFMS)
- Compare reactivity of different nucleophiles (OH⁻, HS⁻, Br⁻, I⁻)

What are PFAS?

- Class of fluorinated surfactants used in aqueous film forming foam (AFFF), polymers, semiconductors, etc.
- Recalcitrant, persistent, and ecologically toxic
- Common removal techniques include ion exchange (IX) resins, granular activated carbon (GAC) adsorbent, and nanofiltration membranes, but further techniques are needed to destroy the resulting PFAS concentrates

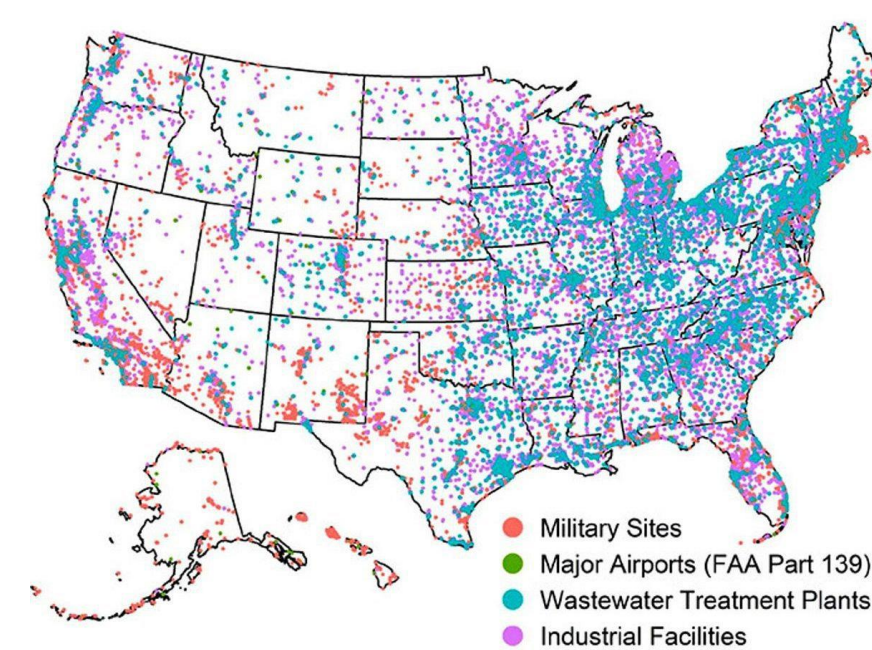


Figure A: PFAS pollution map

Technical Approach

Hydrothermal alkaline treatment (HALT):

- Near-supercritical temperatures (200-374°C) and high pressures (2-22 MPa) create a highly reactive environment
- Strong base (typically sodium hydroxide) breaks carbon-fluorine bonds, which results in defluorination that destroys PFAS

Methods and Procedures:

- 0.01 M TFMS stock solution in water
- 0.1 M nucleophile stock solutions (Figure B)
 - Nucleophiles with different strengths were chosen based on literature values (higher nucleophilicity value is stronger)
- Varying reaction times (30, 60, 90, 180 minutes) at 350°C
 - Heated fluidized sand bath (Figure E)
- Performed in 316 stainless steel Swagelok tube reactors (Figure G)
- Fluoride measured with Fluoride Ion Selective probe (Figure F)

Nucleophile	Nucleophilicity (n)
Sodium bromide	3.89
Sodium hydroxide	4.20
Potassium iodide	5.04
Sodium hydrosulfide	5.10

Figure B: Nucleophilicity strength table



Figure E: Fluidized sand bath (heat source)



Figure F: FISE Probe

Figure G: Tube reactor

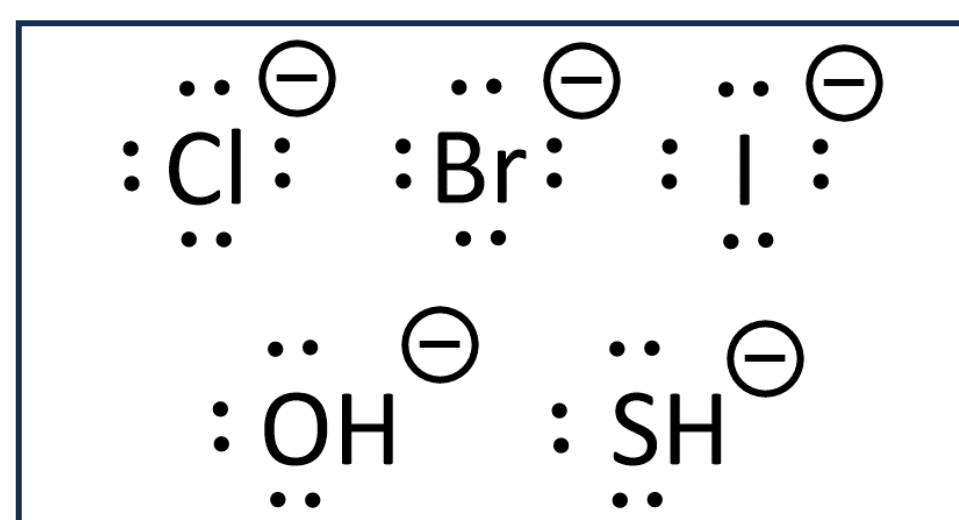


Figure C: Nucleophile structures

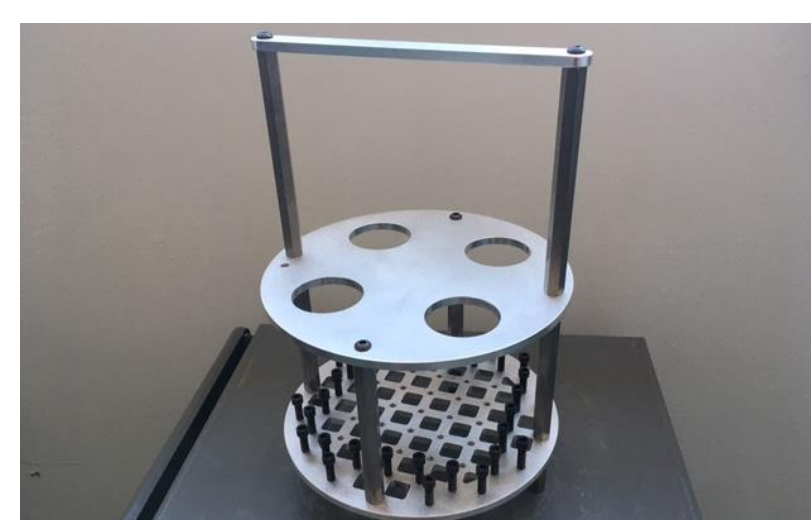
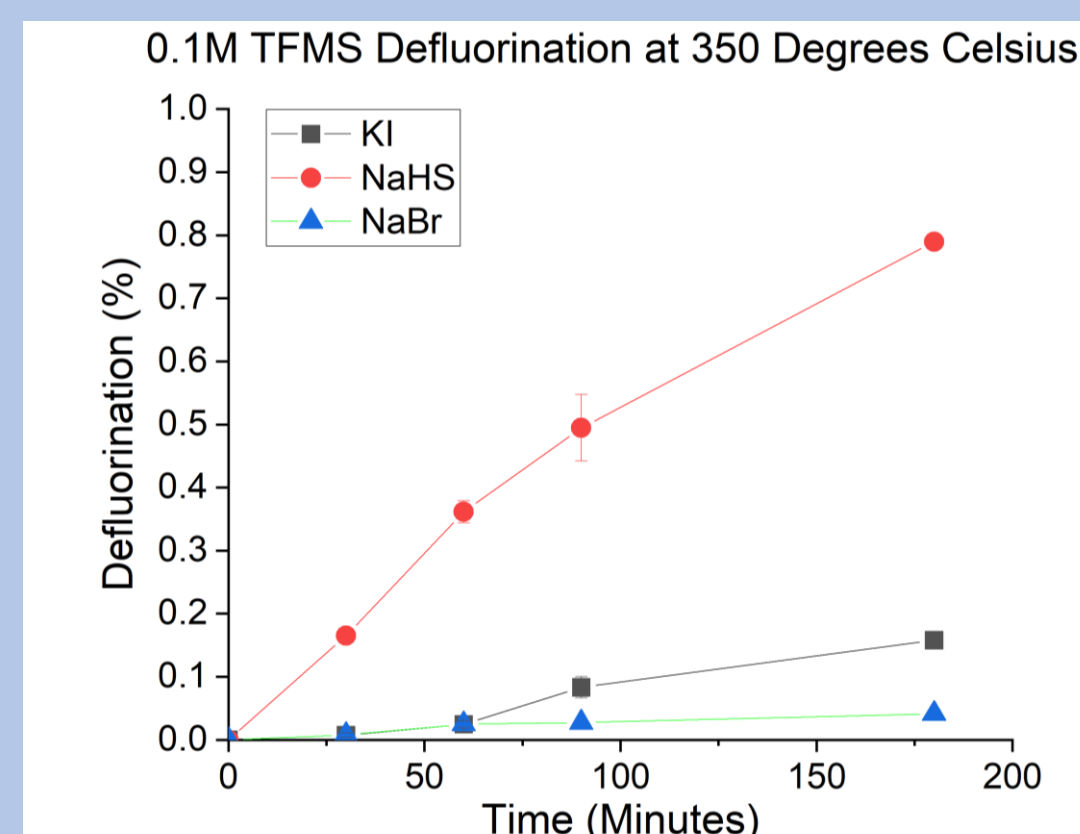


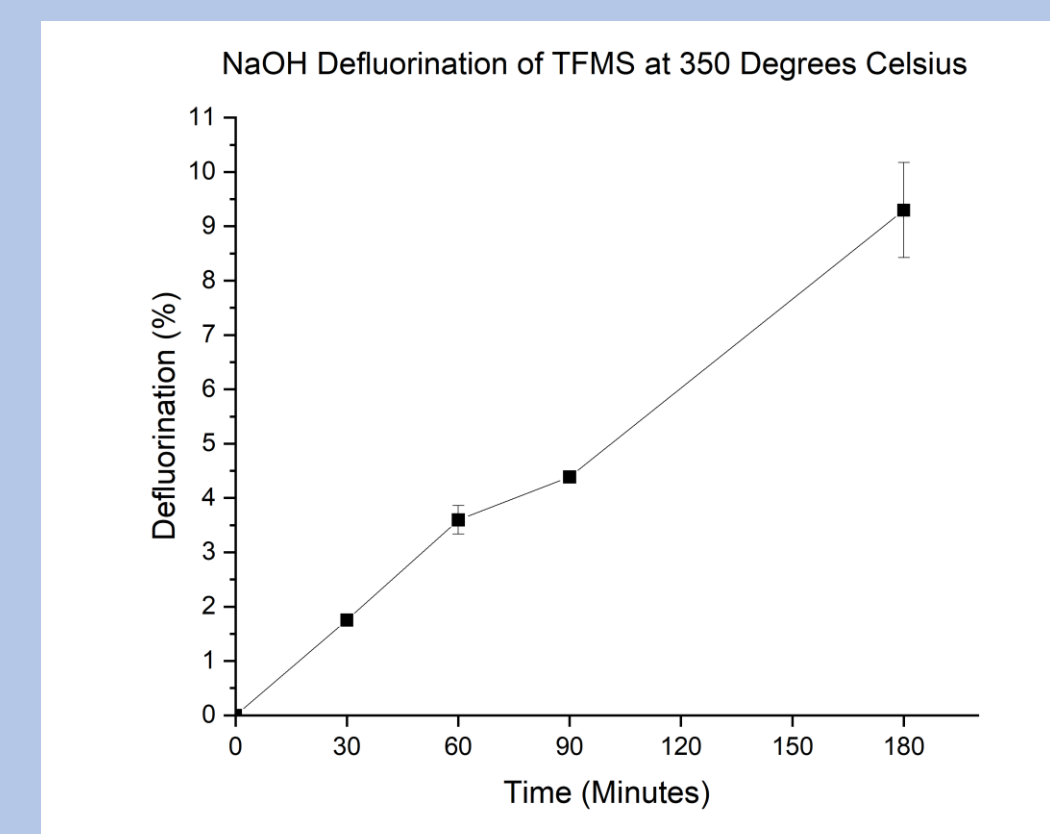
Figure D: Reactor stand

Results

TFMS Defluorination with Different Nucleophiles



TFMS Defluorination with Sodium Hydroxide



Figures H and I: Sodium hydroxide (NaOH) promotes over ten times greater defluorination than the next best-performing nucleophile, sodium bisulfide (NaHS).

TFMS Defluorination with High NaOH Concentration

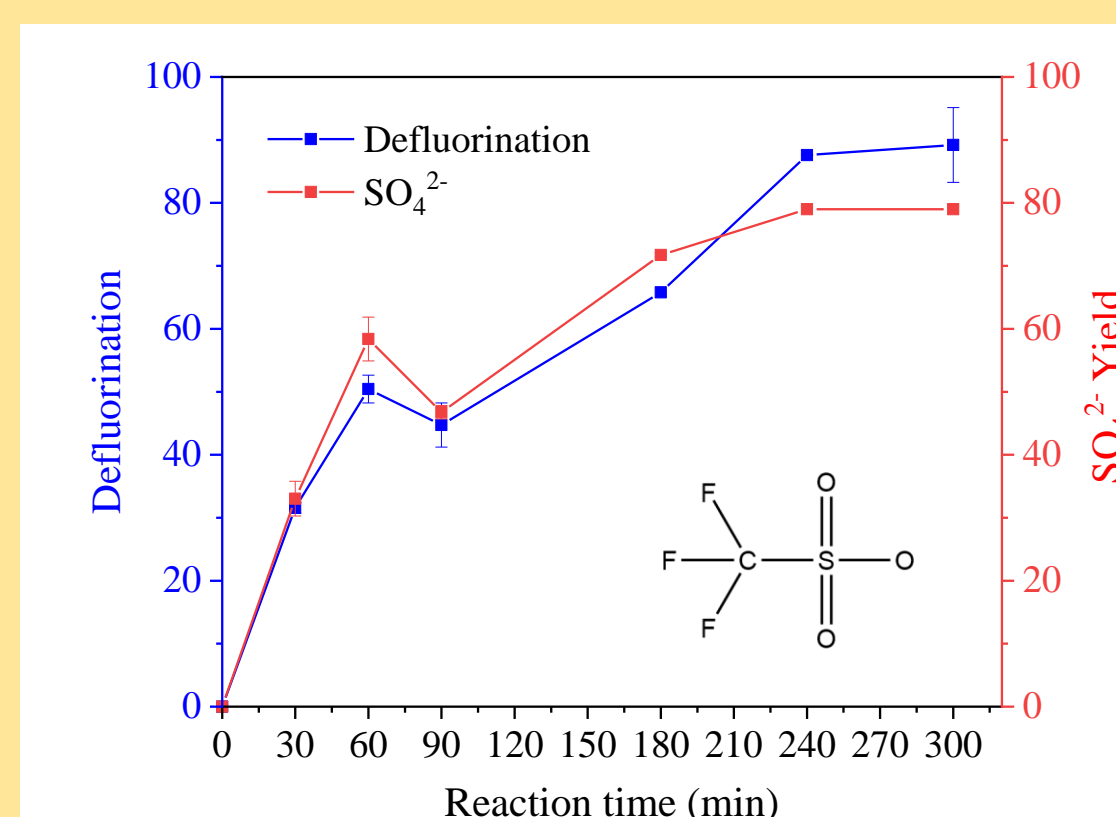


Figure J: TFMS defluorination and sulfite concentration with 1M NaOH at 350°C.

Proposed Defluorination Reaction Mechanism

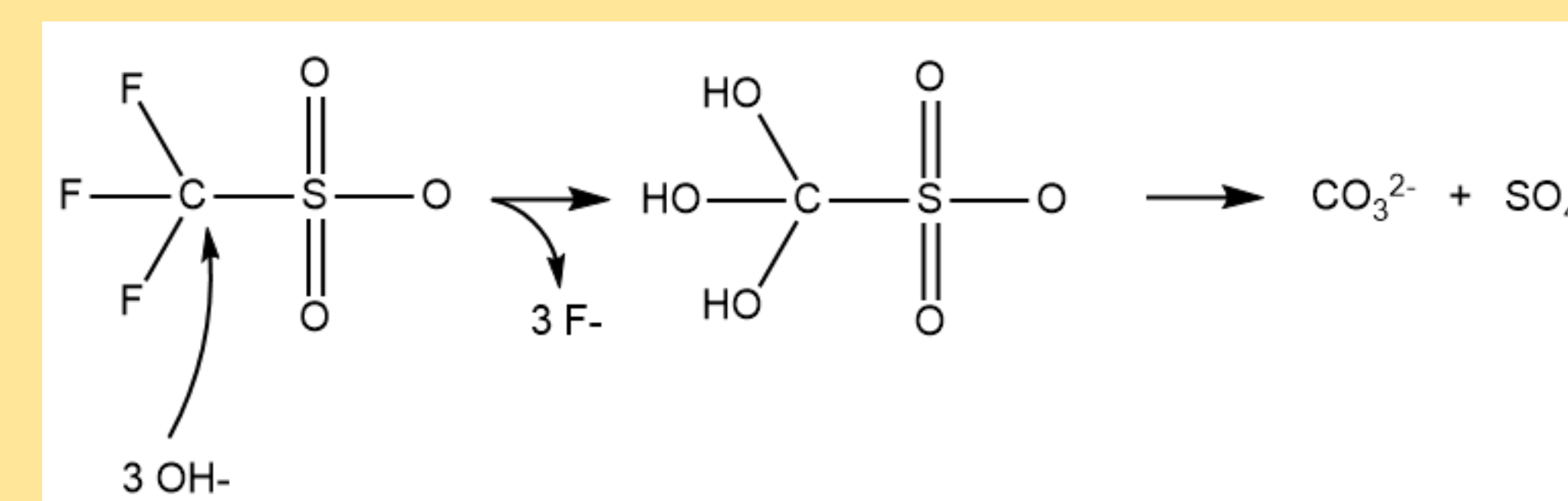


Figure K: Nucleophilic substitution reaction flowchart. Fluoride ions are measured using FISE.

Key Findings

- Sodium hydroxide promotes the most defluorination of short chain TFMS, confirming prior experimental results with long-chain PFAS
- Defluorination does not directly correlate with nucleophilicity values
- Further tests using liquid chromatography-mass spectrometry (LC-MS/MS) to determine intermediate compounds and nuclear magnetic resonance (NMR) imaging to more precisely measure inorganic fluorine
- Further research into using HALT to destroy BTEX co-contaminants (benzene, toluene, ethylbenzene, and xylene) that often appear alongside PFAS in waste streams

Acknowledgements

This work was supported by Strategic Environmental Research and Development Program (ER18-1501), the Strathmann Research Group, and the Mines Summer Undergraduate Research Fellowship (SURF).