

# **Environmental Fate and Effects of Fluorochemicals**

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Environmental Science & Assessment Group*

## **Environmental Issues of Fluorochemicals**

- What are "fluorochemicals"?!?!
- How are they made and used?
- What are the environmental issues?
- What has been done to address the issues?
- What are we doing now to address the issues?
- Where are we going from here?



### Electrochemical Fluorination Cell Products

Desired Product: Perfluorooctanesulfonyl Fluoride (POSF, FX-8)



Also Get-

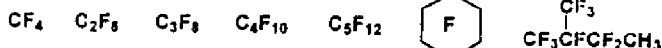
- Other Straight Chain Perfluoroalkyl Products of Various Chain Lengths



- Branched Chain Perfluoroalkyl Products of Various Chain Lengths

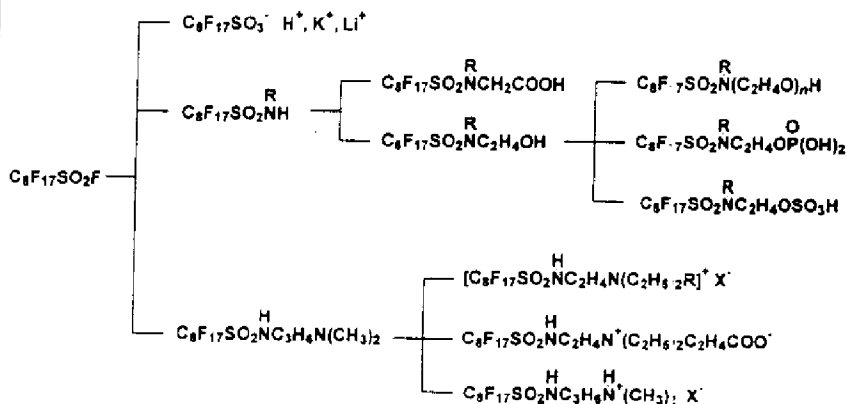


- Other Straight Chain, Branched, and Cyclic Perfluoroalkyl Compounds



- Tars\* and Other By-Products Such As SF<sub>6</sub>

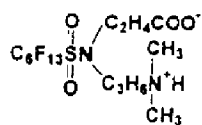
### Fluorochemical Products & Intermediates



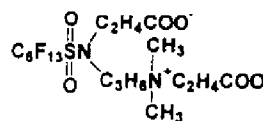
R.A. Guenther, R.A. and Victor, M.L. Surface active materials from perfluorocarboxylic and perfluorosulfonic acids. *I&EC Product Research and Development* 1 (1962) 165-169.

### Example: Surfactant used in AFFF Products

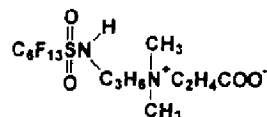
- Three Major Components



"L-4640"



"Diadduct"



- Perfluoro Moiety Primarily Six Carbons Long

### Electrochemical Fluorination Cell Products - Issues

- Mixtures of Unknown Composition
  - ~80% straight chain
  - ?% branched of same chain length
  - ?% straight chain of different length
  - ?% branched chain of different chain lengths
- Lot-to-Lot Variability in Composition
  - by cell run
  - by location (Antwerp ≠ Cordova ≠ Cottage Grove ≠ Decatur)
- What Do You Test?
  - Products as they are sold?
  - Specific compounds extracted from the mixture?
  - Do you test the impurities? Which ones?

### **Nomenclature An *Enormous* Issue**

- Experimental Chemical
  - "L-4640" for AFFF
  - "L-1223" for general surfactant use (e.g. cleaning products)
- MSDS
  - Group Number 04-6084-0; 3M ID 98-0211-5617-3
  - "Amphoteric Fluoroalkylamid Derivative Trade Secret"
- Toxicology Services
  - T-2816
- PMNs - "PMN Substance"
- Chemical Abstracts Service Registry Number
- Product Development Lab
  - "Acrylic Foamer" or "The Foamer" or "New Foamer" or "Old Foamer"
- Environmental Laboratory
  - Use "L-Number"
  - May use Environmental Laboratory "Lab Request Number"

### **Environmental Issues of Fluorochemicals**

- Halogenated
- Persistent
- Widely Dispersed in the Environment
- Potential to Bioaccumulate
- Biologically Active

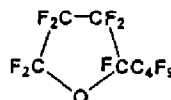
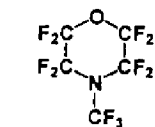
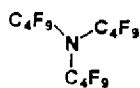
## Atmospheric Issues

### Extensive Program to Evaluate Atmospheric Fate and Effects of 3M Fluorochemicals as CFC and Halon Replacements

- Experimental
  - IR Spectra
  - UV Cross Sections
  - Hydroxyl Radical Reactivity
  - Singlet Oxygen Reactivity
- Data Analysis
  - Radiative Effects
  - Global Warming Potential

## Atmospheric Issues

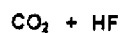
### CFC and Halon Replacement Candidates

C<sub>4</sub>F<sub>10</sub>C<sub>5</sub>F<sub>12</sub>C<sub>6</sub>F<sub>14</sub>

## Atmospheric Issues

### CFC and Halon Replacement Candidates

#### Highly Fluorinated Ethers HFE 401



~5 years for product

## Atmospheric Issues of Perfluorinated Compounds

### Ozone Depletion Potential

CFC-11 = 1

Perfluorochemical = 0

CFC-113 = 0.8

1,1,1-TCE = 0.1

### Atmospheric Lifetime

Perfluorochemicals = 5,000 years

1,1,1-TCE = 5.4 years

### Global Warming Potential

$\text{CO}_2 = 1$

$n\text{-C}_4\text{F}_9\text{OCH}_3 = 300$

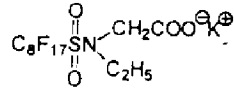
$\text{C}_3\text{F}_{12} = 4,100$

$\text{C}_6\text{H}_{14} = 7,400$

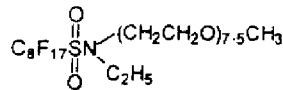
CFC-11 = 4,000

1,1,1-TCE = 110

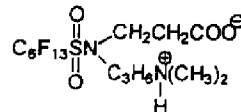
### Aerobic Biodegradation Results



37% ThOD in 6.25 hrs. at 30  
O<sub>2</sub> uptake

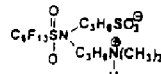
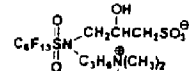
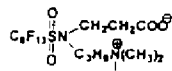
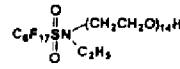
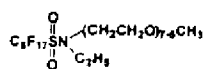
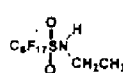
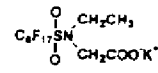
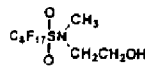
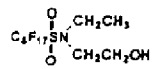


25 to 33% in 2 days  
DOC removal



6% in 5 days  
CO<sub>2</sub> production

### Aerobic Biodegradation of Fluorochemicals





**Research at Michigan State University**

**Dr. Craig Criddle  
Blake Key**

**NSF Center for Microbial Ecology and  
Department of Civil and Environmental Engineering**

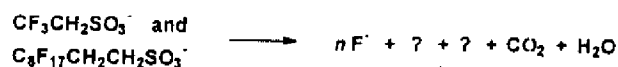
**Research at Michigan State University**

**Multichamber Microcosms**

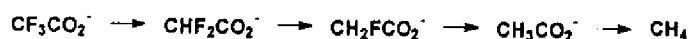
- **Fermenting**
- **Acetogenic**
- **Methanogenic**
- **Sulfidogenic**
- **Denitrifying**
- **Aerobic**



## Recent Results

At MSU: Aerobic and Anaerobic Systems

- several volatile degradation products
- fluoride released concentration dependent

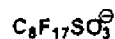
At USGS in Menlo Park, Calif.: Anaerobic Systems

## Light Water™ AFFF Usage Wastes

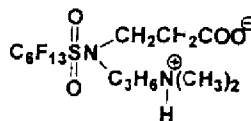
- Continuing Issue with Customers
  - Fire Fighting Training Sites
  - Fire Protection Equipment Testing
  - Accidental Discharge by Automatic Equipment
  - Simple Operation and Maintenance Required
- Potential Environmental Harm
  - Fish Kills
  - Bird Exposure
  - Disruption of Wastewater Treatment Plants
- Potential Negative Publicity for the Corporation

## Major Components of 3M AFFF Products

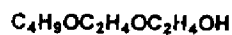
1% "Filmer" FC-95



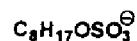
3% "Acrylic Foamer" L-4640



20% Butyl Carbitol

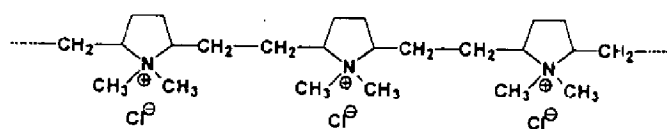


8% Octyl Sulfate



## AFFF Waste Treatment

## Cationic Polyelectrolytes



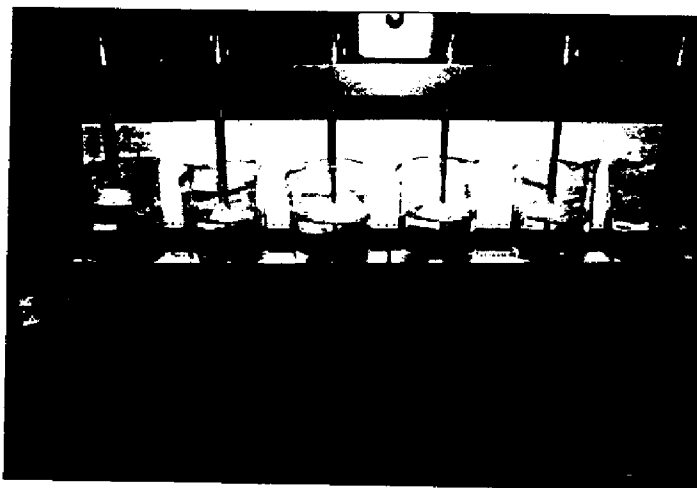
MW ~ 200,000 Daltons

~ 160 Daltons

Calgon Merquat 100

## **AFFF Waste Treatment**

- 1. Addition of Cationic Polyelectrolyte**
- 2. Flocculation**
- 3. Separation**
  - Precipitation**
  - Centrifugation**
  - Sand Filtration**
  - Reverse Osmosis/Ultrafiltration**
- 4. Discharge of Treated Water**
- 5. Disposal of Polymer/Surfactant Precipitate**
  - Incineration**
  - Landfill**



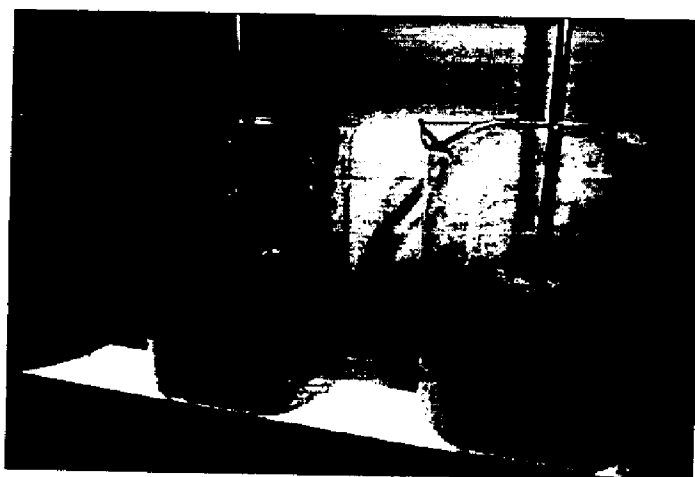
*Environmental Laboratory*

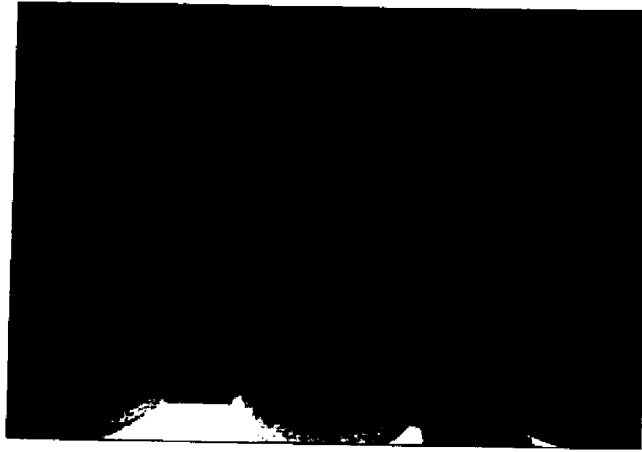
**3M**



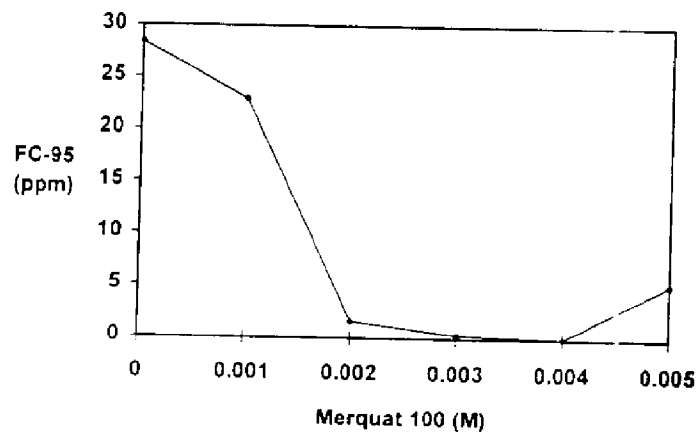
*Environmental Laboratory*

**3M**

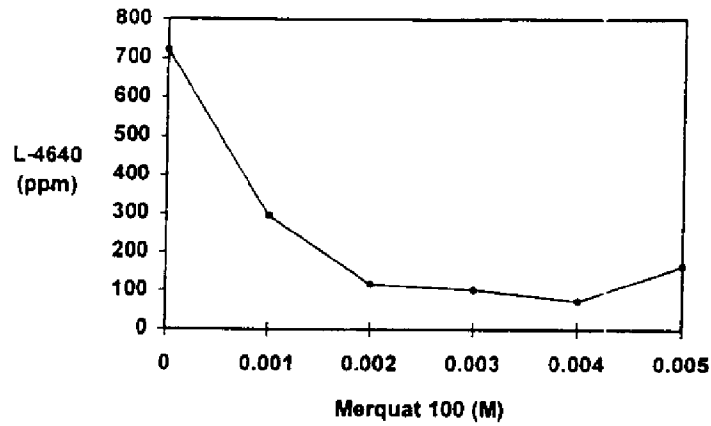




### Effect of Cationic Polymer Concentration



**Effect of Cationic Polymer Concentration**



**Fluorochemical Surfactant Removal**

	Concentration in Supernatant (mg/L)	Removal (%)
<b>L-4640</b>		
Nalco 8157	4.9	99.4
Nalco 7735	3.4	99.6
FeCl <sub>3</sub>	2.2	99.7
<b>FC-95</b>		
Nalco 8157	0.67	99.8
Nalco 7735	0.02	99.9
FeCl <sub>3</sub>	0.00	100.0



## **Future Work on AFFF Waste Treatment**

### **Separation Method**

Is precipitation sufficient?

Centrifugation, sand filtration?

Reverse osmosis/ultrafiltration: too costly,  
difficult to operate and maintain.

### **Disposal of Polymer/Surfactant Precipitate**

Incineration of fluorochemicals?

Landfill possible?

### **Seeking Wastewater Treatment Firm for Scale-up**

## **Fluorochemical Bioconcentration in Fish**

### **Uptake Experiment**

25 mg/L ammonium perfluorooctanoate (FC-143)

30 fish/tank

5 fish removed and sacrificed at day 7 and day 13

Analysis by combustion and F<sup>-</sup> analysis by ISE

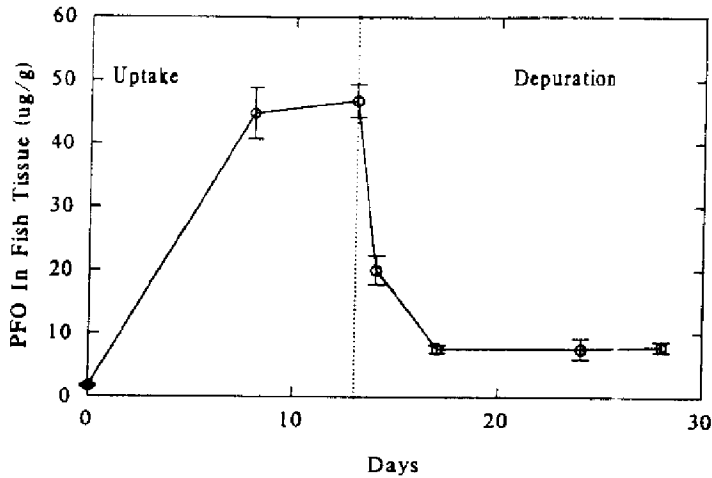
### **Depuration Experiment**

Fish remaining at end of uptake put into fresh  
water

5 fish removed at day 14, day 17, and day 20

Analysis by combustion and F<sup>-</sup> analysis by ISE

**Perfluorooctanoate Bioaccumulation in Fish**



**Perfluorooctanoate Bioaccumulation in Fish**

Bioc... PFO concentration in fish tissue  
PFO concentration in test solution

Time (days)	PFO in Test Solution (ppm)	PFO in Fish Tissue (ppm)	BCF
8	25.5	44.7	1.75
13	25.9	46.7	1.80

Range of concern: 1,000 < BCF < 1,000,000

## Fluorochemical Bioconcentration in Fish

### Accomplishments

- Developed method for fluorochemical concentration in fish by combustion method
- FC-143 report reviewed by Dr. John Giesey, Environmental Toxicology Dept., Michigan State University
- Incorporated recommendations into protocol
- Presented results to customer and at SETAC 1995

### Future Work

- FC-95 (perfluorooctane sulfonate)
- Acrylic foamer (L-4640)
- Ethyl FOSE alcohol
- Others as necessary

## Fluorochemical Products - Issues

- Analytical Procedures are Extremely Difficult
  - Hindered by the number of components
  - Techniques/methods valid for one component probably won't work for other components
    - Charged vs. uncharged
    - Positive charge vs. negative charge vs. zwitterionic/amphoterics
  - What matrix?
    - Soil - sand, clay, loam, compost, ...
    - Water - sewage sludge, wastewater, drinking water, sea water, groundwater, ...
    - Animal - rabbit, rat, human, fish, cockroach, ...
    - Tissue - blood, liver, skin, hair, ...
    - Food - pizza, popcorn, food simulating liquid, ...
    - Plant - corn, algae, ...
    - Atmosphere
    - Product

**Fluorochemical Products - *Issues***

- Analysis of Fluorochemicals in Environmental Samples NOT Impossible
- Tremendous Developments Since ~1993
  - Extraction Techniques
  - Separation Techniques
    - GC, HPLC, Supercritical Fluid Extraction, and many others
  - Detection Techniques
    - Mass Spectrometry, FID, PID, FTIR, and many others
  - Automated Sample Handling and Instrument Control to Maximize Throughput
- GLP Methods in Place for Several Fluorochemicals in Several Matrices
  - Including blood, livers, skin, and other animal tissues
- Non-GLP Methods in Place for Several Fluorochemicals in Several Matrices
  - Wastewater sludge, soil, drinking water, air, and others
- Can Detect Any Fluorochemical in Any Matrix

**Fluorochemical Products - *Issues***

- Tremendous Quantities of Fluorochemicals Being Produced
  - Tens or hundreds of millions of pounds/year
  - Don't know production quantities of competitors
  - Don't know their chemistries
- Effects on Biosphere Unknown
  - Human health?
  - Other living creatures?
- Human Health and Environmental Studies are
  - Extremely Difficult
  - Extremely Expensive
- Ultimate Environmental Fate Unknown
- Unknown Liability

**Fluorochemical Products - Issues**

- **Product Composition**
  - Unknown
  - Not Critical to Product Use
- **Products meet certain QC specifications**
  - Boiling Point (Fluorinert Products)
  - Surface Tension (Fluorad Products)
  - Oil & Water Repellancy (Scotchban & Scotchgard Products)
  - Extinguishment (Light Water Products)
  - Other physical/chemical properties as appropriate to meet specifications
- **End Use May Be Unknown**
  - Don't know who buys them
  - Don't know what kinds of products they are used in

**Fluorochemical Steering Committee**

Charles Cowman	<i>Specialty Chemicals Division</i>
Thomas Dipasquale	<i>Legal</i>
Craig Olson	<i>Chemical, Film and Allied Group Compliance</i>
Sik-Toh Ting	<i>Fluorochemical Technology Center</i>
Paul Ackerman	<i>Specialty Materials Division</i>
Larry Zoebel	<i>Medical Department</i>
John Butenhoff	<i>Toxicology Services</i>
Dale Bacon	<i>Environmental Laboratory</i>
James Sugg	<i>Industrial Hygiene Services</i>
Don Theissen	<i>Corporate Product Responsibility</i>
Lael Pickett	<i>Specialty Chemicals Division</i>
Craig Burton	<i>Fluorochemical Technology Center</i>

**Fluorochemical Technical Advisory Committee**

Craig Burton	<i>Fluorochemical Technology Center</i>
Craig Olson	<i>Chemical, Film and Allied Group Compliance</i>
Jim Johnson	<i>Environmental Laboratory</i>
Roger Perkins	<i>Toxicology Services</i>
Steve Gordon	<i>Toxicology Services</i>
Jeff Mandel	<i>Medical Department</i>
Robert Howell	<i>Environmental Laboratory</i>
John Marhevka	<i>Corporate Research Laboratory</i>
Stan Sorenson	<i>Industrial Hygiene Services</i>
V. Prothapragada	<i>Specialty Materials Division</i>

**Fluorochemical Work in Progress**

- New Product Testing (Evaluate 2/week & Test 3/month)
- PMNs (2 - 4/year)
- Water Solubility (e.g. Ethyl FOSE Alcohol)
- FC-129 Degradation Study
- HFE 401 & HFE 402 - Fish, *Daphnia*, Algae
- Michigan State Research Biodegradation
- FC-845 Process Wastewater Ecotox (*Daphnia* & Fish)
- Method Development - Ongoing for different compounds and matrices
- Pesticide Working Group
- Bioconcentration (FC-143, FC-95, Ethyl FOSE, and others)
- GLP Tox Studies Underway ( e.g. Dermal Transport)
- Degradable Fluorochemical Building Blocks
- Proposals
  - Soil Sorption
  - Comparison of Extinguishment with AFFF vs. Non-Extinguishment